Supporting information

PEG_{400}-enhaced synthesis of *gem*-dichloroaziridines and *gem*-dichlorocyclopropanes through the dichlorocarbene in situ generated

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Typical Procedure for the Preparation of Imines

Benzaldehyde (3.18 g, 30 mmol) and aniline (2.79 g, 30 mmol) were dissolved in ethanol (50 mL). After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure. Purification of the residue by recrystallization in Et_2O/hexane gave pale-yellow N-benzylideneaniline (**2a**); yield: 4.35 g (80%).

N-benzylideneaniline (1a).[30] Pale yellow solid, mp 50-51 °C (lit.,[30] mp 51-52 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H, C*H*), 7.94-7.91 (m, 2H), 7.50-7.41 (m, 3H), 7.43-7.39 (m, 2H), 7.27-7.22 (m, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 160.4, 152.0, 136.2, 131.4, 129.1, 128.82, 128.75, 125.9, 120.8 ppm; GC-MS (EI, 70 eV) m/z (%) 182 (12), 181 (M^+, 88), 180 (100).

N-benzylidene-4-methoxyaniline (1b).[30] Gray solid, mp 71-72 °C (lit.,[31] mp 69-70 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H, C*H*), 7.91-7.89 (m, 2H), 7.48-7.46 (m, 3H), 7.24 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 3H, OCH_3) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.4, 158.3, 144.8, 136.4, 131.1, 128.7, 128.6, 122.2, 114.4, 55.5 ppm; GC-MS (EI, 70 eV) m/z (%) 211 (M^+, 92), 196 (100).

N-benzylidenenaphthalen-1-amine (1c).[32] Bright yellow solid, mp 74-75 °C (lit.,[32] mp 76.1 °C; lit.,[33] mp 73-75 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H, C*H*), 8.36-8.34 (m, 1H), 8.01-7.99 (m, 2H), 7.84-7.82 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.50-7.42 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 160.3, 149.3, 136.4, 133.9, 131.4, 129.0, 128.8, 127.6, 126.4, 126.0, 125.8, 125.7, 124.0, 112.7 ppm; GC-MS (EI, 70 eV) m/z (%) 232 [$(M+1)^+$, 17], 231 (M^+, 100), 230 (86), 154 (21), 128 (17), 127 (53).

N-(4-methylbenzylidene)aniline (1d).[30] Light yellow solid, mp 40-41 °C (lit.,[34] mp 41-42 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H, *H*C=N), 7.77 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.7, 153.7, 143.3, 135.1, 130.9, 130.5, 130.2, 127.2, 122.3, 23 ppm; GC-MS (EI, 70 eV) m/z (%) 195 (M^+, 83), 194 (100), 180 (4), 91 (15), 77 (50).

N-(4-chlorobenzylidene)aniline (1e).[30] Light yellow solid, mp 62-63.5 °C (lit.,[31] mp 63-64 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H, *H*C=N), 7.85 (d, *J* = 8.4 Hz, 2H), 7.47-7.44 (m, 2H), 7.42-7.38 (m, 2H), 7.27-7.25 (m, 1H), 7.23-7.21 (m, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.7 (H*C*=N), 151.6, 137.3, 134.6, 129.9, 129.1, 129.0, 126.2, 120.8 ppm; GC-MS (EI, 70 eV) m/z (%) 217 (31), 216 (45), 215 (M^+, 98), 214 (100).

N-(4-nitrobenzylidene)aniline (1f).[35] Light yellow solid, mp 89-90 °C (lit.,[36] mp 92-93 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H, *H*C=N), 8.33 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.46-7.42 (m, 2H), 7.32-7.28 (m, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 157.3, 150.9, 149.3, 141.6, 129.4, 129.3, 127.1, 124.0, 120.9 ppm; GC-MS (EI, 70 eV) m/z (%) 227 (11), 226 (M^+, 72), 225 (36), 197 (13), 196 (95), 195 (100).

General procedure for the synthesis of *gem*-dichloroaziridines

To a mixture of PEG_{400} (60.0 mg, 15 mol%), sodium hydroxide powder (120.0 mg, 3.0 mmol) and imines **1** (1.0 mmol), chloroform (2.0 mL) was added. The reaction mixture was stirred for 30 min at room temperature. The system was washed with ether. The combined solvent was concentrated using a rotary evaporator to afford the crude product. Purification by column chromatography on neutral Al_2O_3 (eluting with petroleum ether/ethyl acetate) to provide the desired products.

2,2-dichloro-1,3-diphenylaziridine (2a).[9] Pale yellow solid, mp 98.5-100 °C (lit.,[9] mp 100-102 °C; lit.,[37] mp 98-99 °C); IR (KBr) ν/cm^{-1} 3035, 2921, 1603, 1526 (C=C, Ar), 693, 574; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.55 (m, 2H), 7.49-7.45 (m, 3H), 7.42-7.38 (m, 2H), 7.21-7.18 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.9 132.9, 129.1, 128.9, 128.4, 127.8, 124.3, 119.7, 75.2, 54.6 ppm; GC-MS (EI, 70 eV) m/z (%) 230 (7), 229 [$(C_{14}H_{11}{}^{37}ClN)^+$, 32], 228 (16), 227 [$(C_{14}H_{11}{}^{35}ClN)^+$, 99], 194 (9), 193 [$(C_{14}H_{11}N)^{2+}$, 60].

2,2-dichloro-1-(4-methoxyphenyl)-3-phenylaziridine (2b). Colorless solid, mp 86-87 °C (lit.,[38] mp 90 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.45-7.41 (m, 3H), 7.03-7.00 (d, *J* = 2.6 Hz, 2H), 6.93-6.89 (d, *J* =

2.6 Hz, 2H), 3.81 (s, 3H), 3.67 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 156.6, 138.2, 133.0, 128.8, 128.4, 127.8, 120.7, 114.4, 75.9, 55.5, 54.5 ppm; GC-MS (EI, 70 eV) m/z (%) 259(20), 258 [$(C_{15}H_{13}{}^{37}ClNO)^{2+}$, 11], 257 (59), 223 [$(C_{15}H_{13}NO)^{2+}$, 100], 222 (47).

2,2-dichloro-1-(naphthalen-1-yl)-3-phenylaziridine (2c).[2] Red solid, mp 115-116 °C (lit.,[2] mp 120-121 °C); IR (KBr) ν/cm^{-1} 3055, 2968, 1586, 1505 (C=C), 1458, 1401, 1271, 1067, 954, 870, 804, 779, 763, 695, 575, 549; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.71-7.60 (m, 5H), 7.48-7.41 (m, 4H), 6.95 (d, J = 7.6 Hz, 1H), 3.97 (s, 1 H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.8 134.1, 132.7, 129.0, 128.5, 128.4, 128.2, 128.0, 126.7, 126.4, 125.4, 125.1, 123.9, 114.0, 53.5 ppm; GC-MS (EI, 70 eV) m/z (%) 277 (19), 243 [$(C_{18}H_{13}N)^{2+}$, 38], 242 (100), 241 (51), 240 (10).

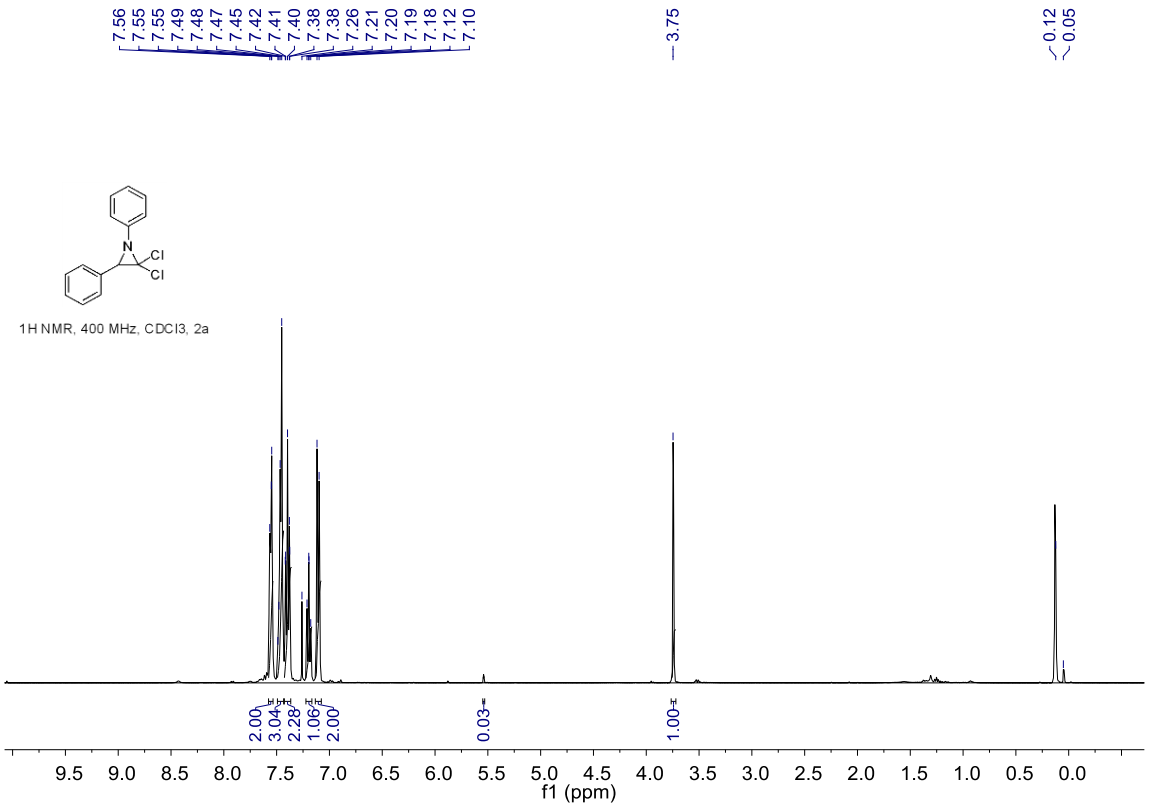
2,2-dichloro-1-phenyl-3-(*p*-tolyl)aziridine (2d).[11] Light yellow solid, mp 74.5-76 °C (lit.,[11] mp 75-76 °C); IR (KBr) ν/cm^{-1} 2922, 2857, 2025, 1506, 1462, 1389, 1277, 1135, 1007, 835, 540; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 4H), 7.24 (m, 1H), 7.18-7.14 (m, 1H), 7.08-7.06 (m, 2H), 3.68 (s, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 145.0 138.9, 130.0, 129.14, 129.06, 127.7, 124.2, 119.7, 75.4, 54.6, 21.3 ppm; GC-MS (EI, 70 eV) m/z (%) 243 (33), 242 [$(C_{15}H_{13}{}^{35}ClN)^{+}$, 18], 241 (100), 207 [$(C_{15}H_{13}N)^{2+}$, 32], 206 (38).

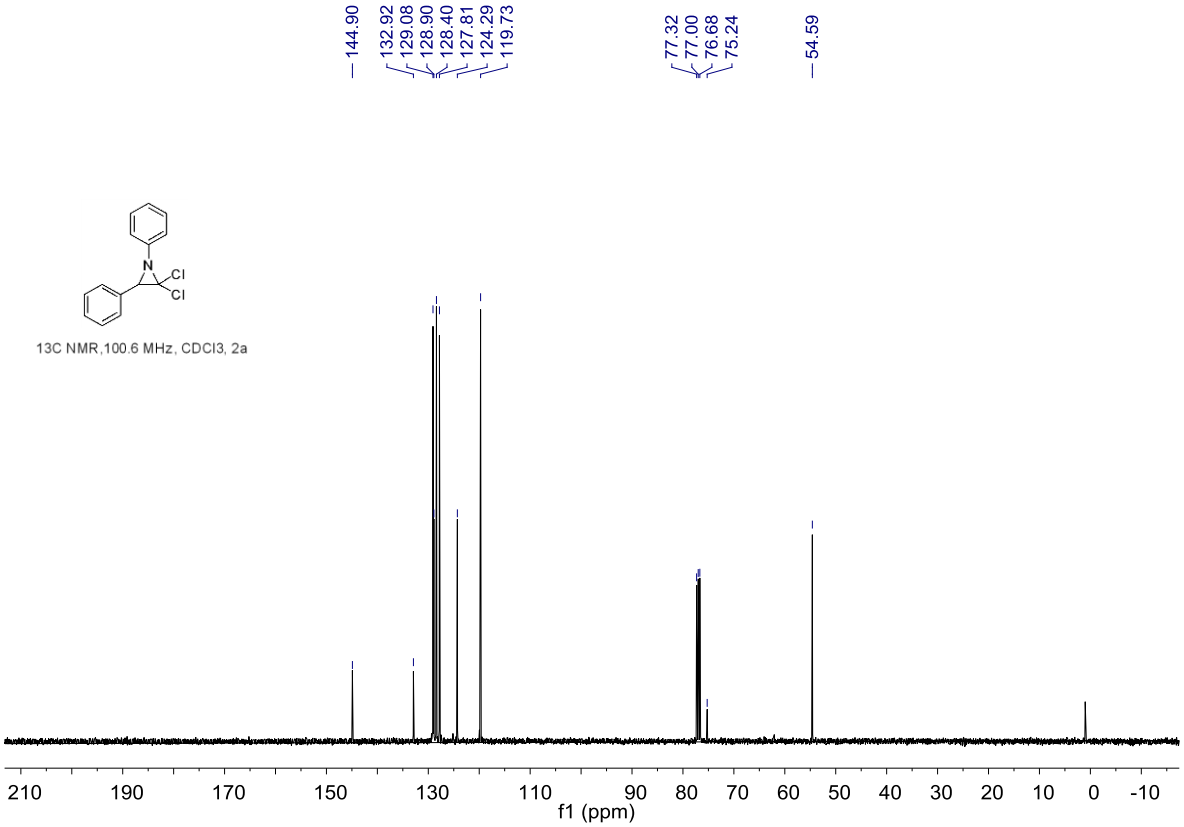
2,2-dichloro-3-(4-chlorophenyl)-1-phenylaziridine (2e).[11] Light yellow solid, mp 84.5-86 °C (lit.,[11] mp 86-87 °C); IR (KBr) ν/cm^{-1} 3040, 2926, 1597, 1492, 1417, 1386, 1303, 1274, 1090, 885, 818, 754, 694, 563; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.37 (m, 6H), 7.21-7.17 (m, 1H), 7.07 (d, J =8.0 Hz, 2H), 3.69 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 144.6, 134.9, 131.5, 129.17, 129.15, 128.7, 124.5, 119.7, 75.0, 53.9 ppm; GC-MS (EI, 70 eV) m/z (%) 263 (69), 261 (100), 229 (14), 228 (20), 227 [$(C_{14}H_{10}ClN)^{2+}$, 41], 226 (47).

2,2-dichloro-3-(4-nitrophenyl)-1-phenylaziridine (2f).[11] Yellow solid, mp 104 °C (lit.,[11] mp 104.5-106 °C); IR (KBr) ν/cm^{-1} 3041, 2945, 1599, 1521, 1494 (C=C), 1348, 891, 815, 758, 693, 566; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.28 (d, J =2.0 Hz, 2H), 7.73-7.69 (d, J = 2.0 Hz, 2H), 7.42-7.37 (m, 2H), 7.23-7.19 (m, 1H), 7.08-7.05 (d, J = 1.6 Hz, 2H), 3.80 (s, 1H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 148.3 144.1, 140.1, 129.3, 128.9, 124.8, 123.7, 119.7, 74.7, 53.5 ppm; GC-MS (EI, 70 eV) m/z (%) 274 ($C_{14}H_9{}^{37}ClN_2O_2$, 25), 272 ($C_{14}H_9{}^{35}ClN_2O_2$, 63), 209 (26), 208 (100), 207 (39).

The charts of ^{1}H and ^{13}C NMR of *gem*-dichloroaziridines 2a-f.

2,2-dichloro-1,3-diphenylaziridine 2a:





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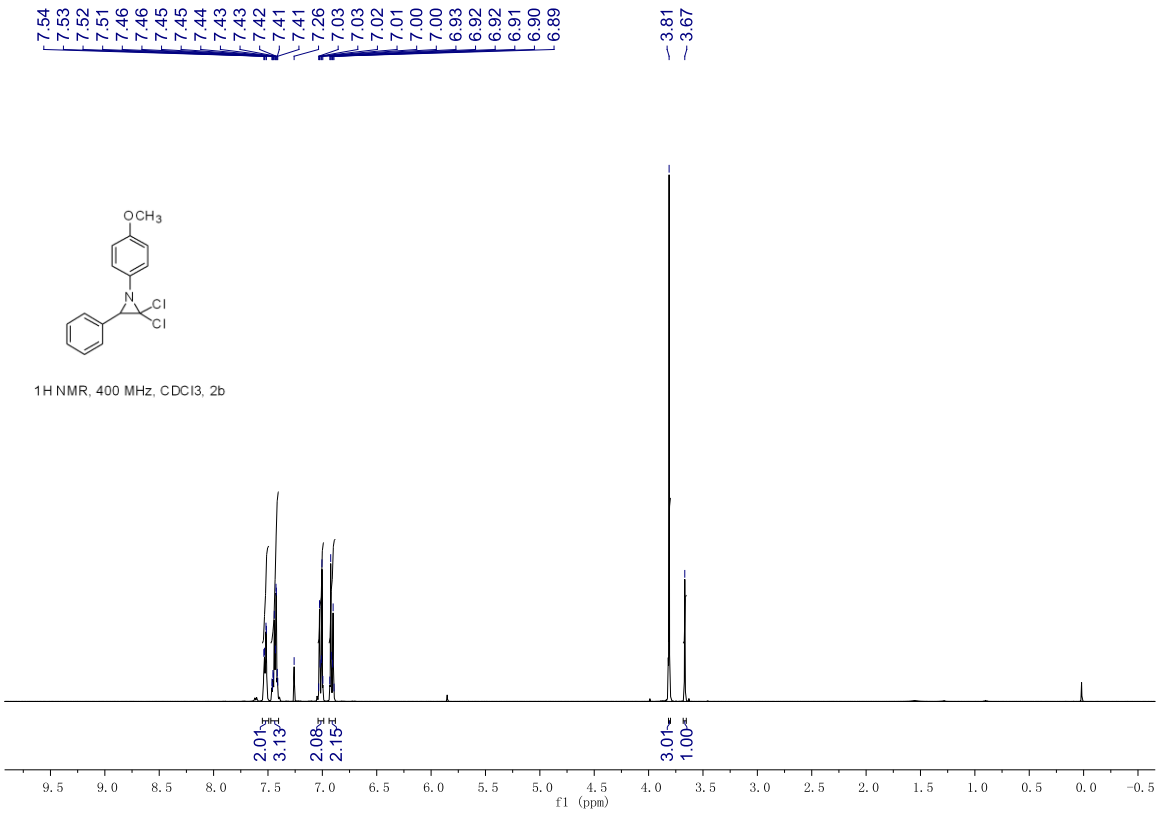

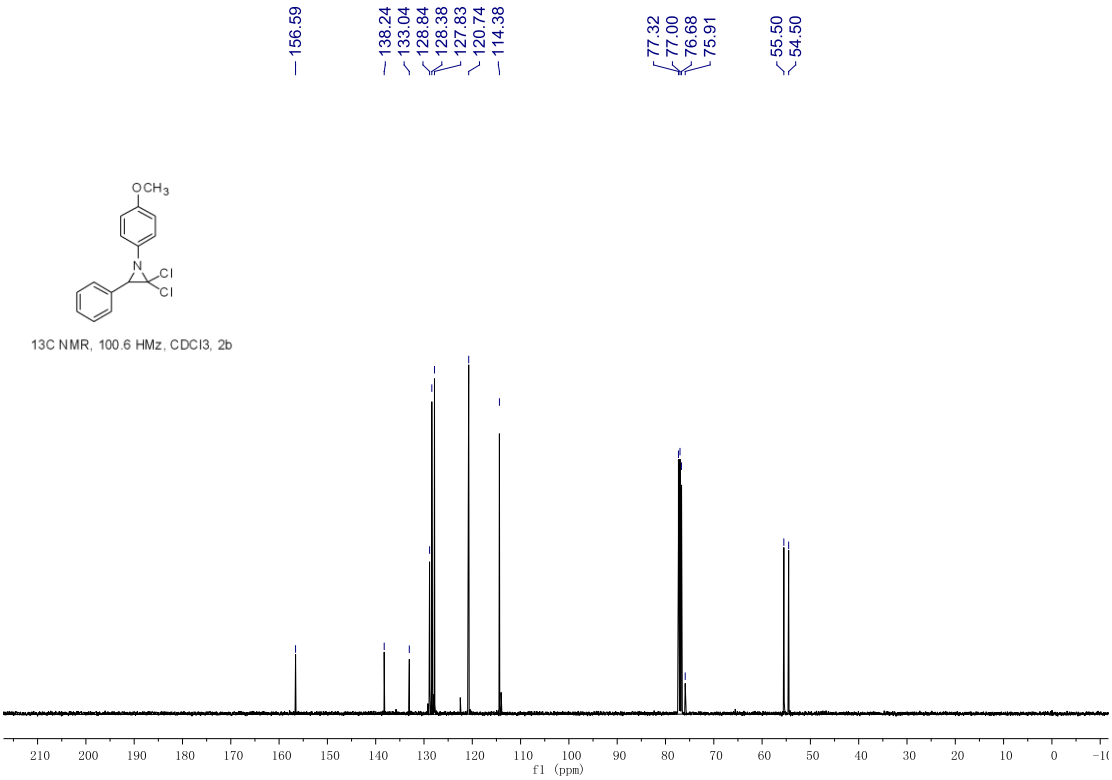

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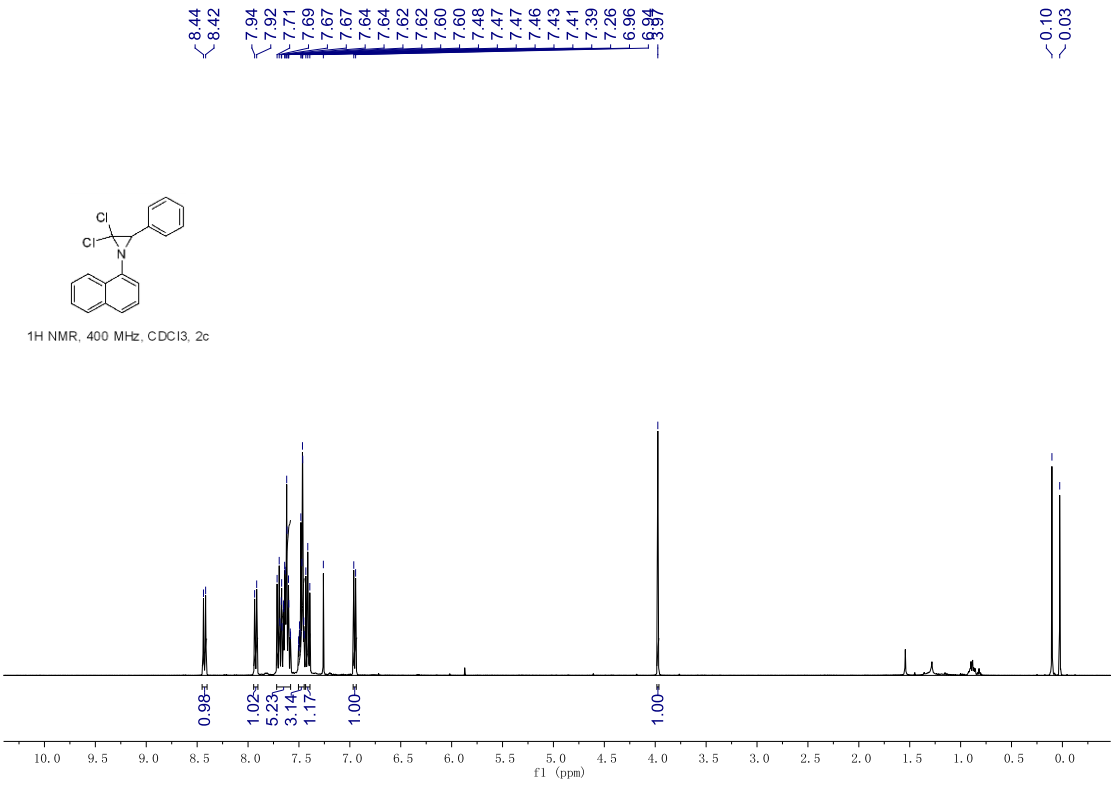
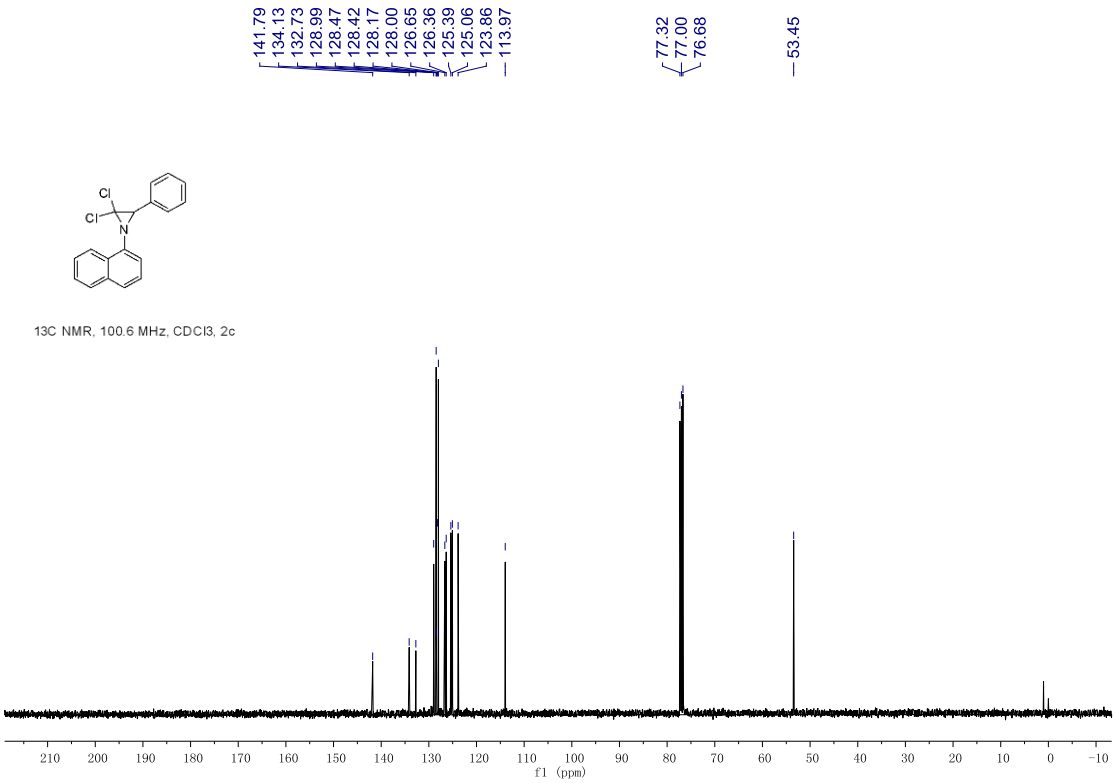
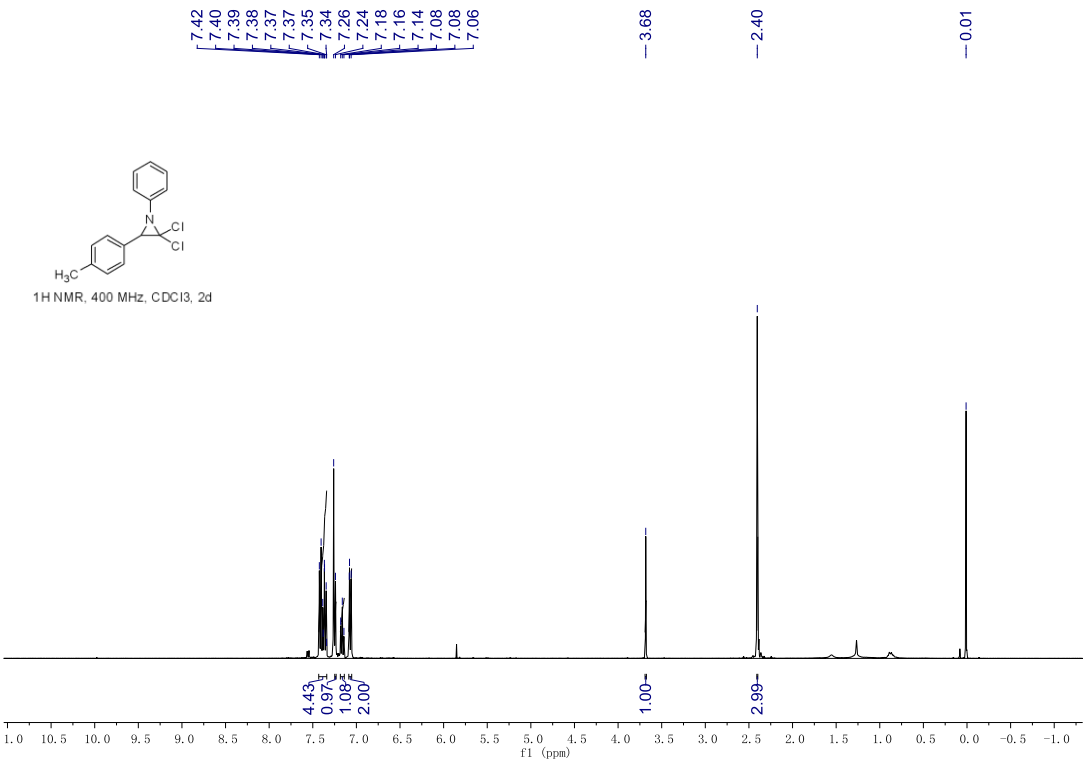
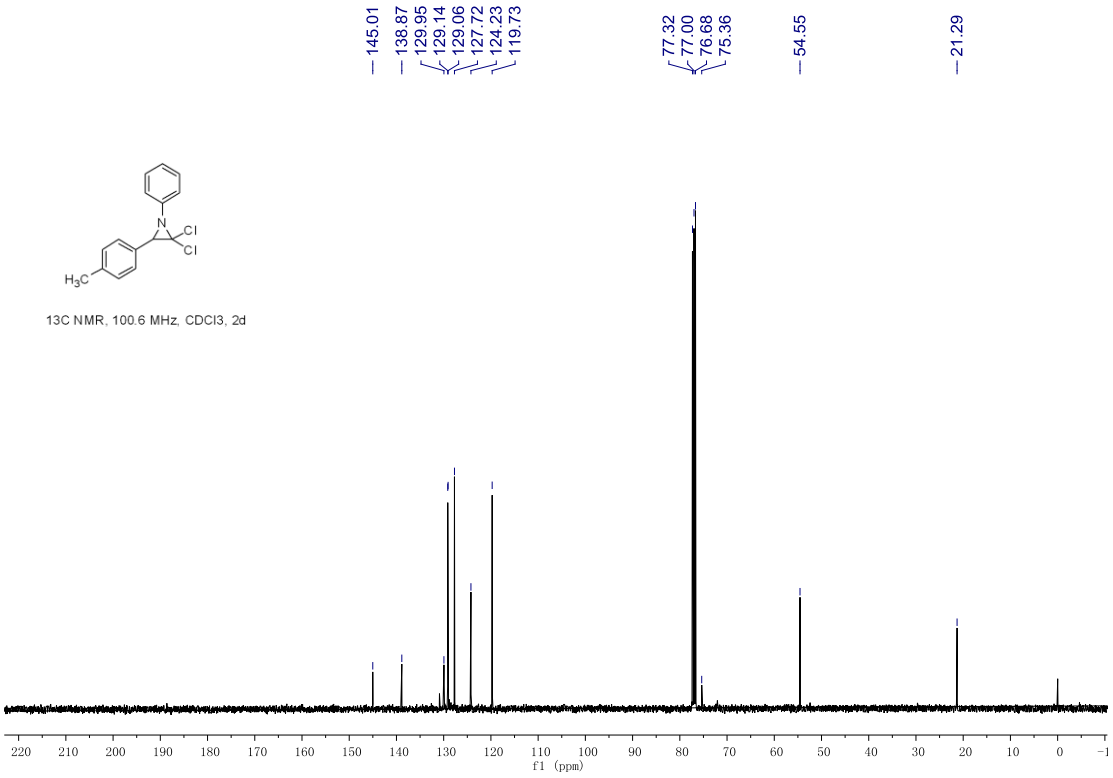




2,2-dichloro-1-phenyl-3-(*p*-tolyl)aziridine 2d:





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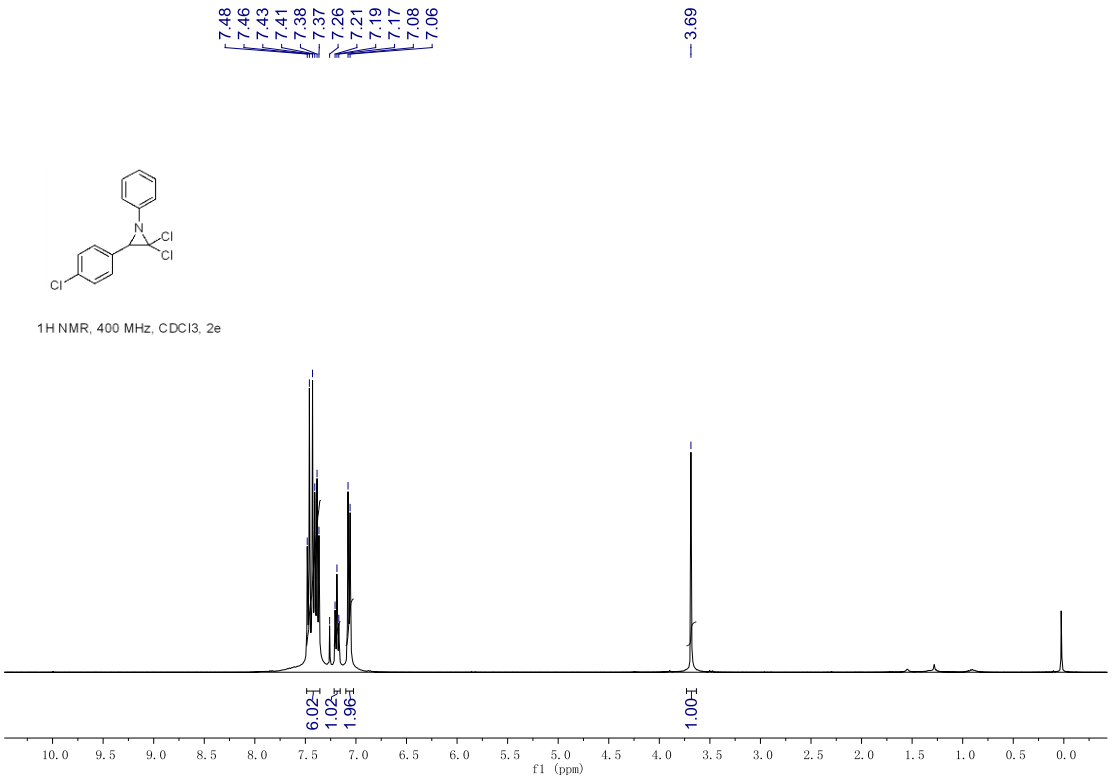

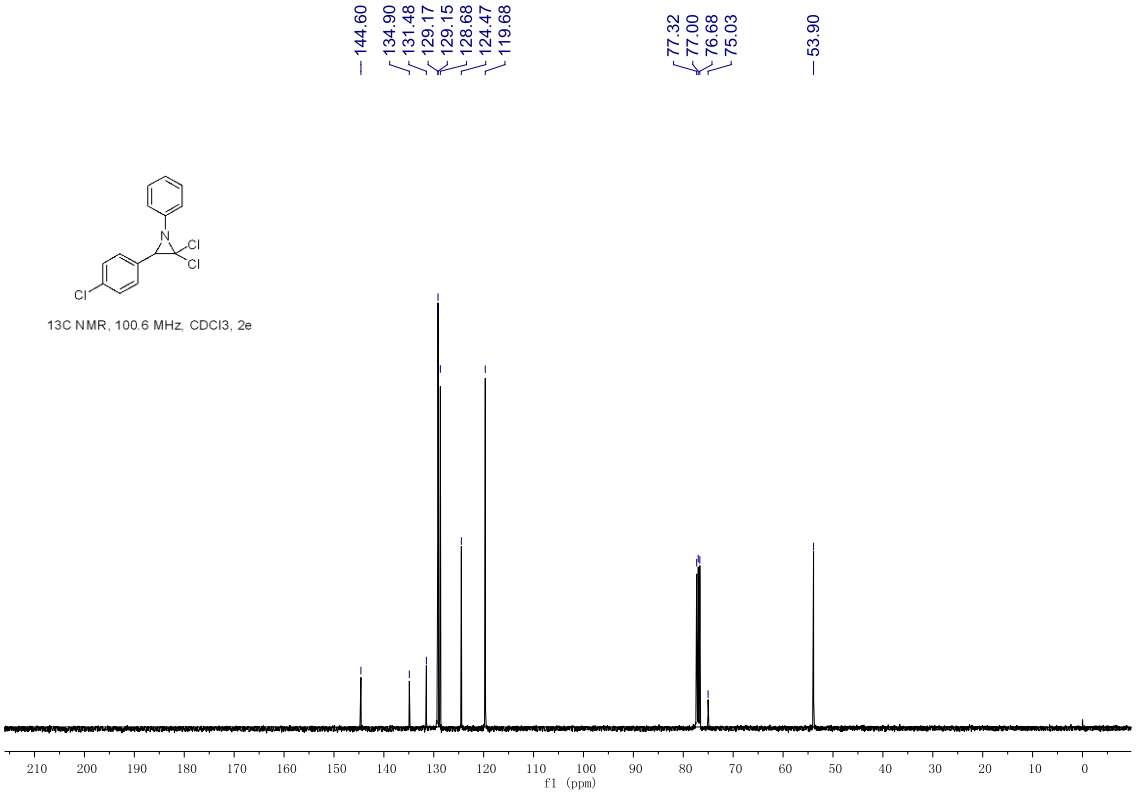

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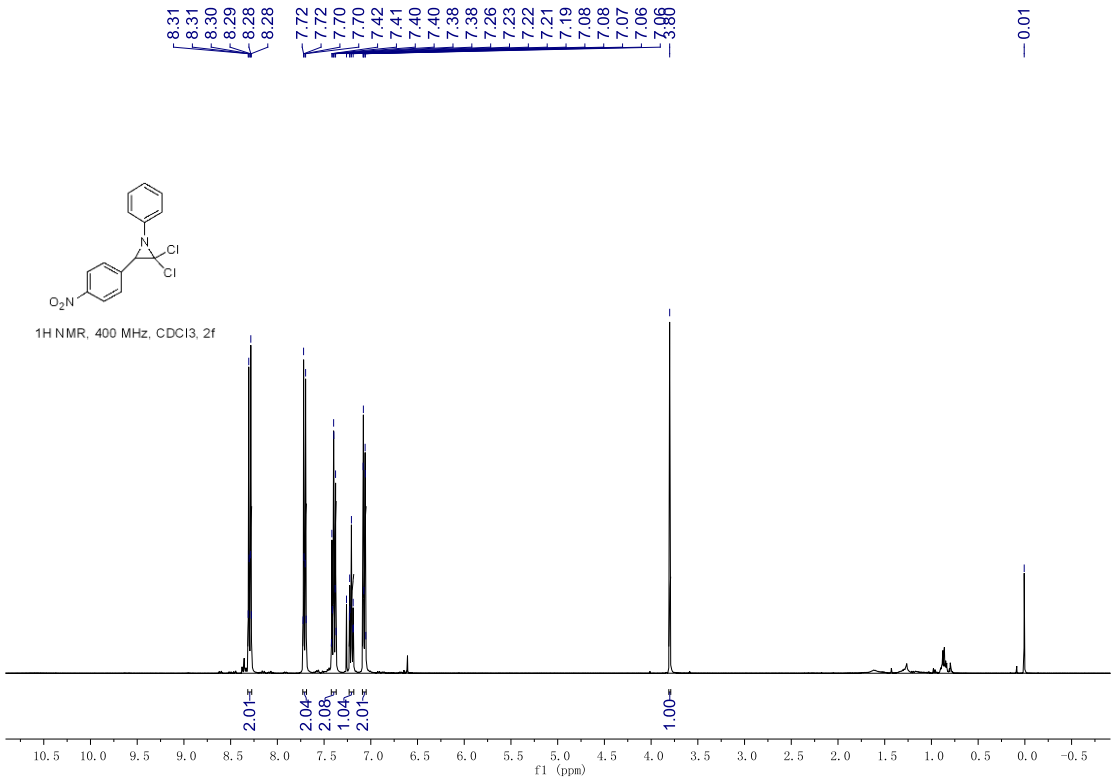
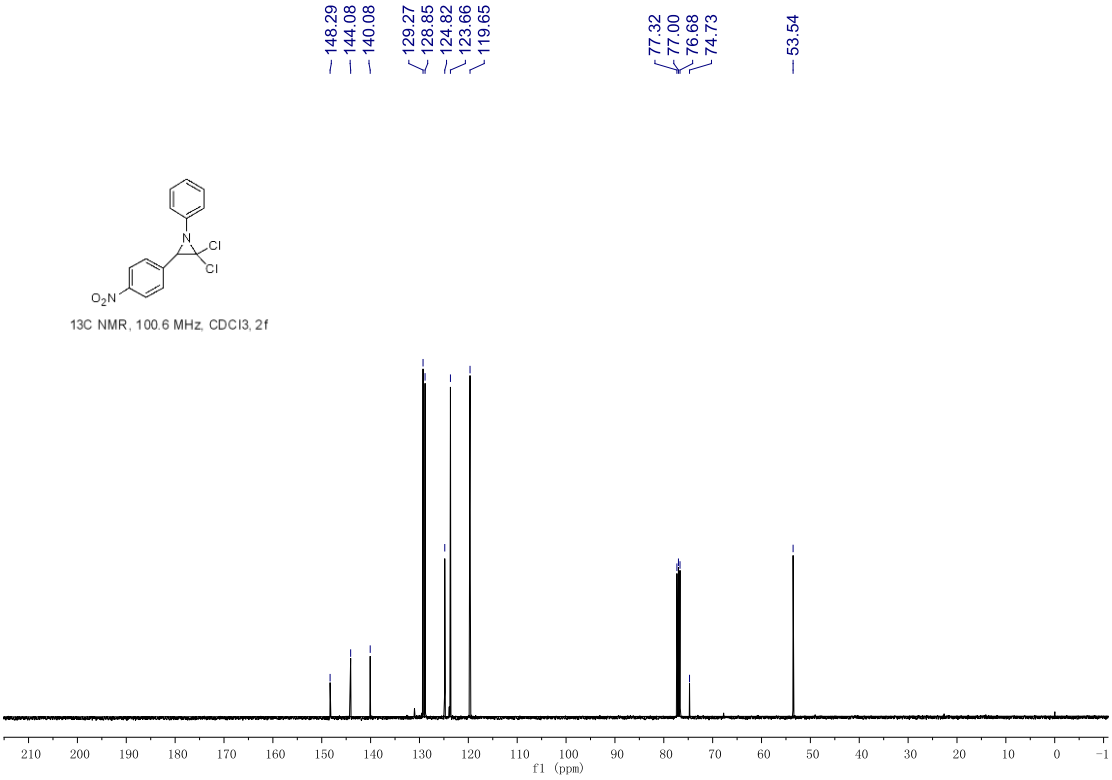
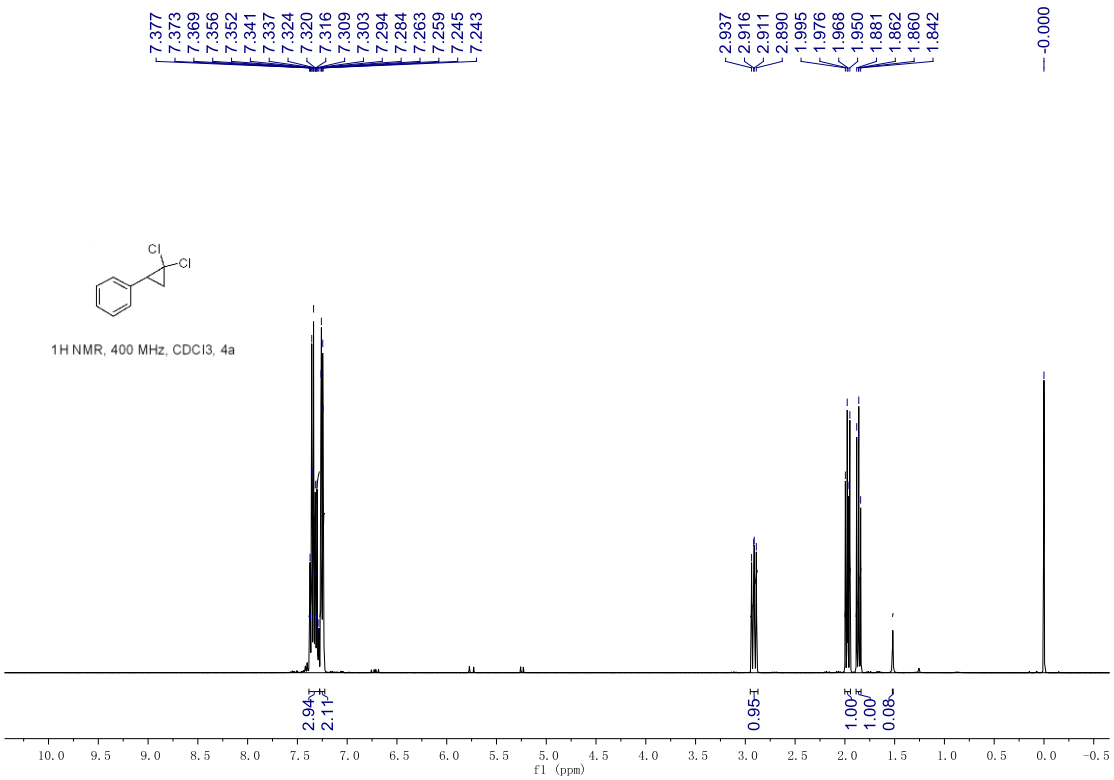
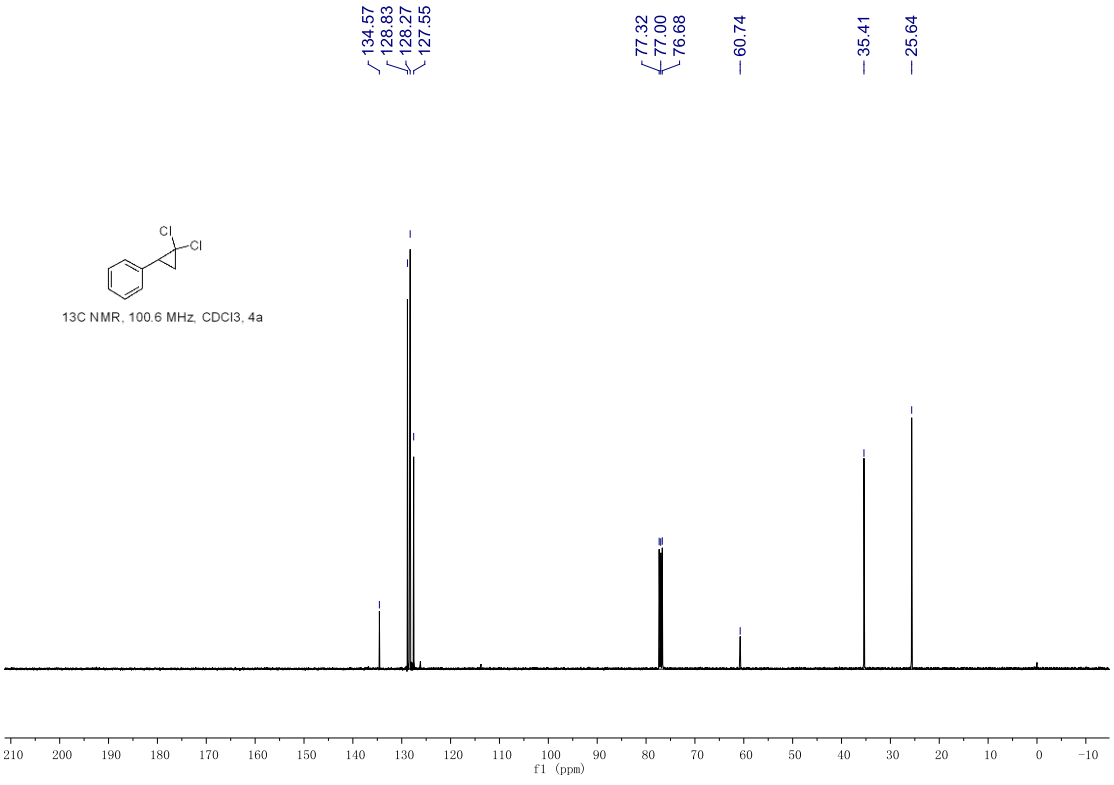




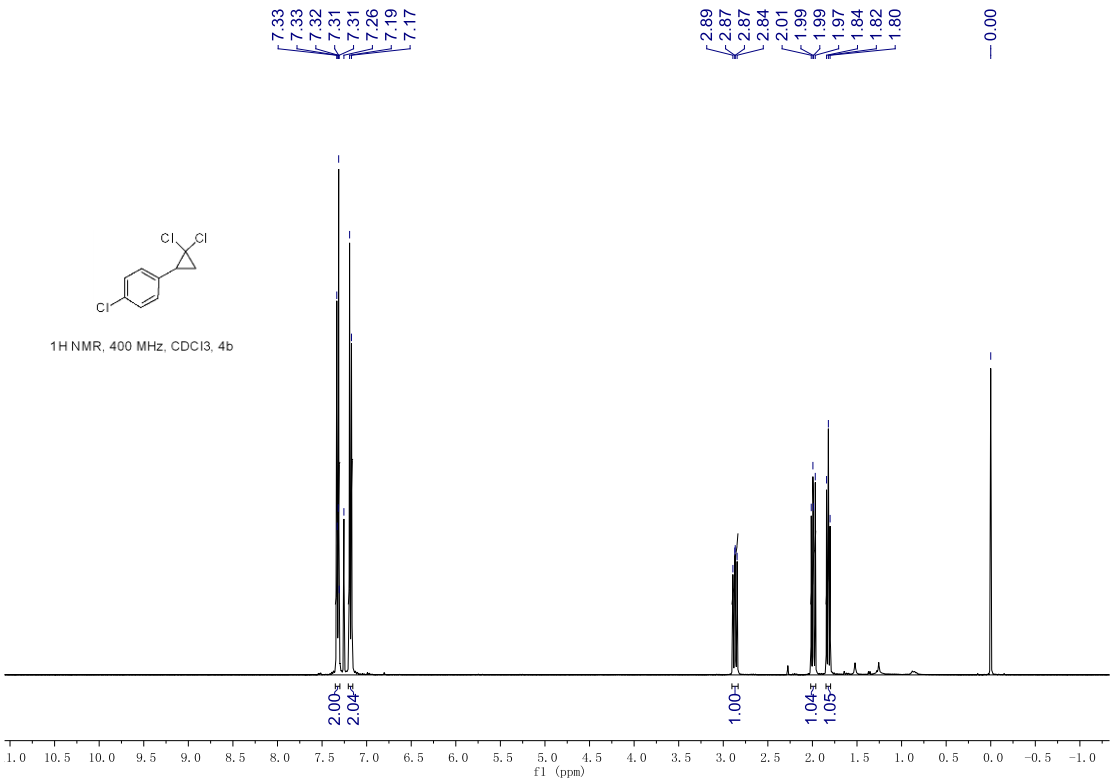
The charts of ^{1}H and ^{13}C NMR of *gem*-dichlorocyclopropanes 4a-f.

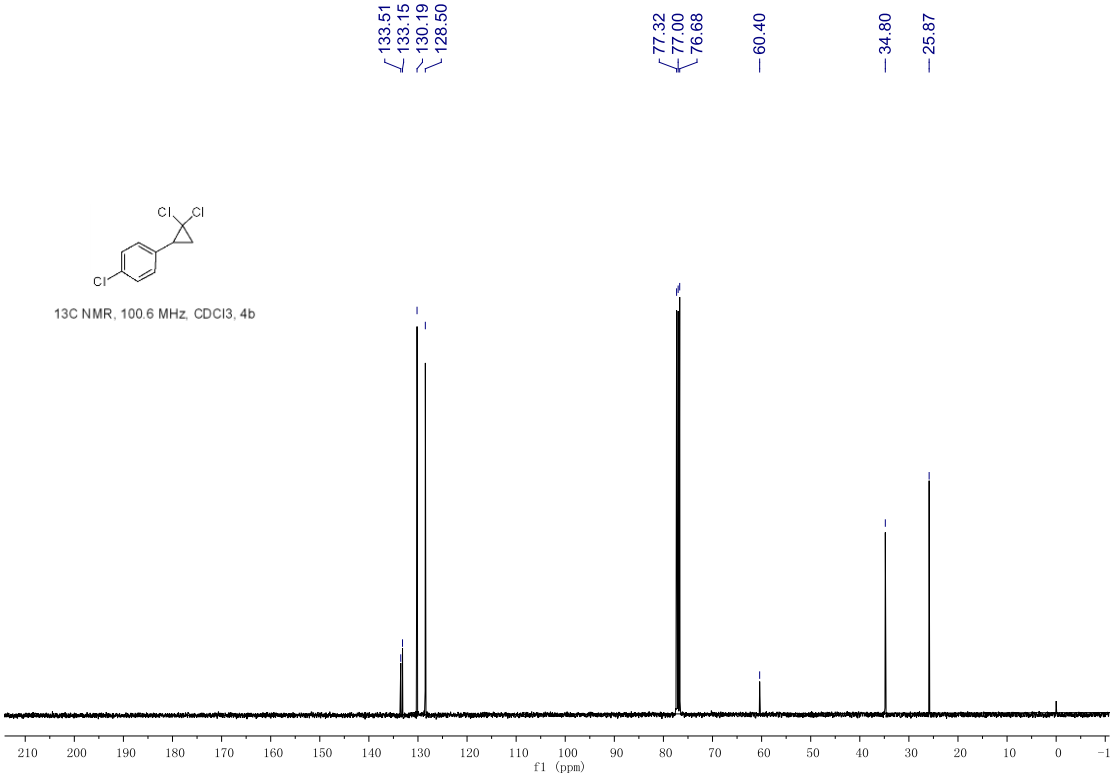
1,1-dichloro-2-phenylcyclopropane 4a:



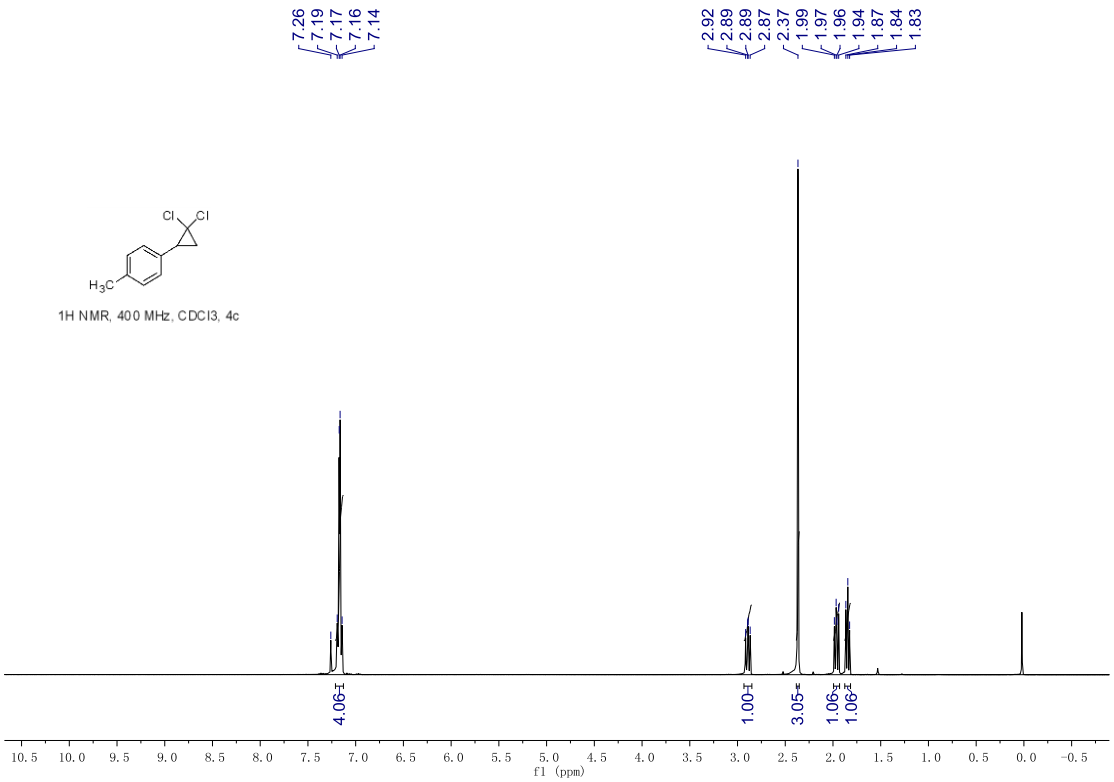


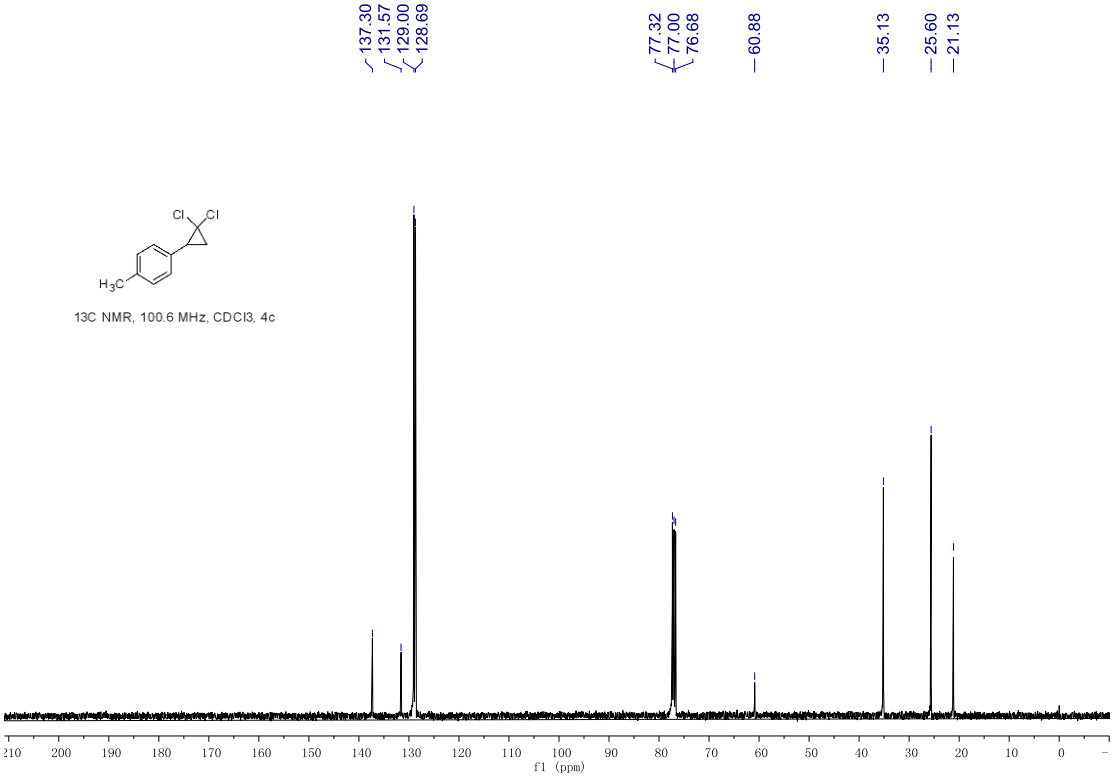
1,1-dichloro-2-(4-chlorophenyl)cyclopropane 4b:



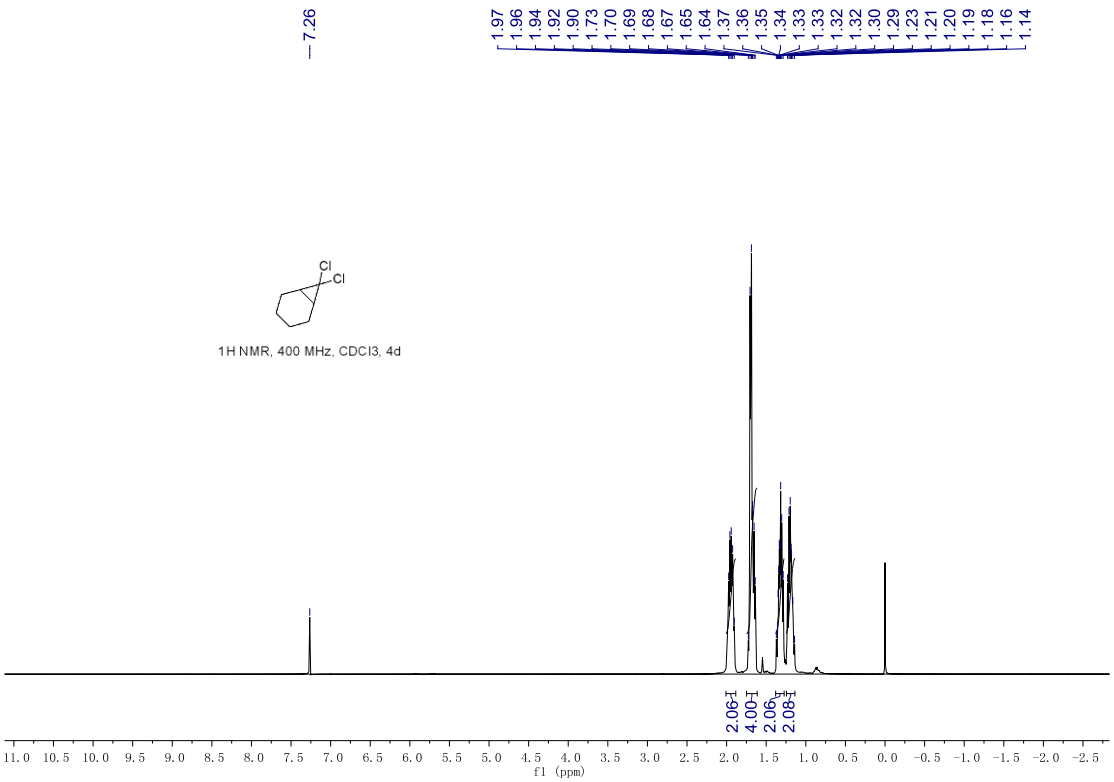


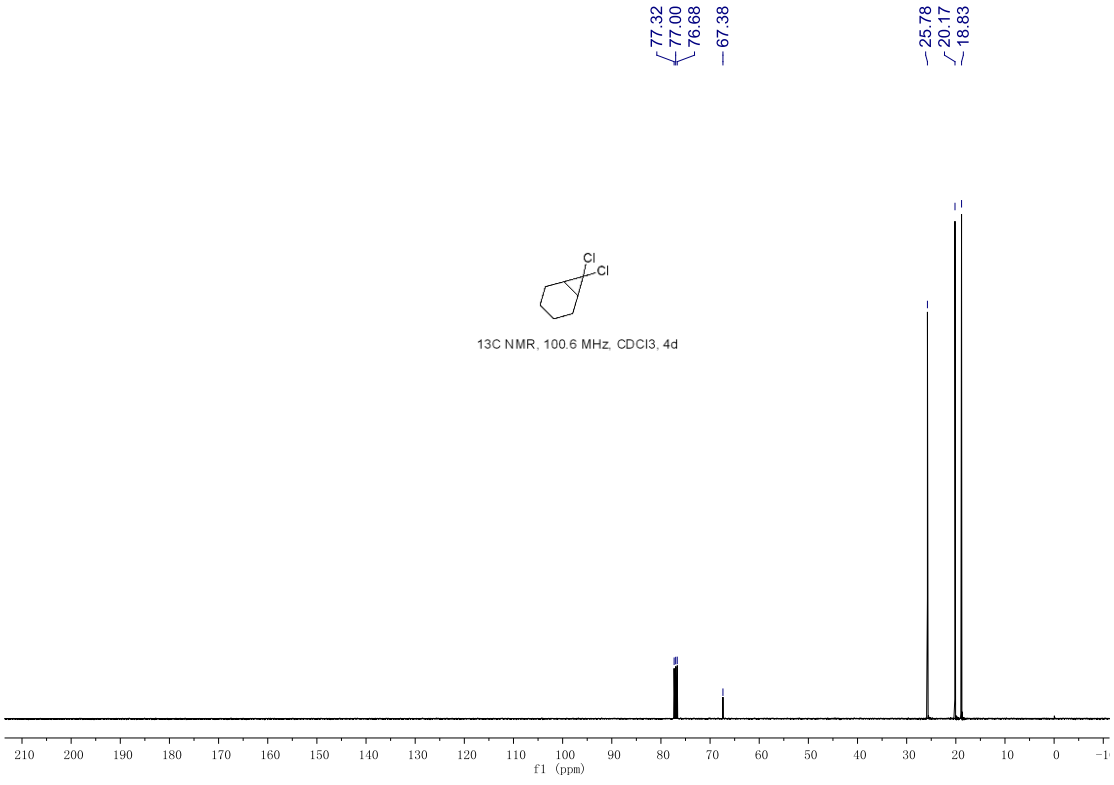
1,1-dichloro-2-(4-methylphenyl)cyclopropane 4c:



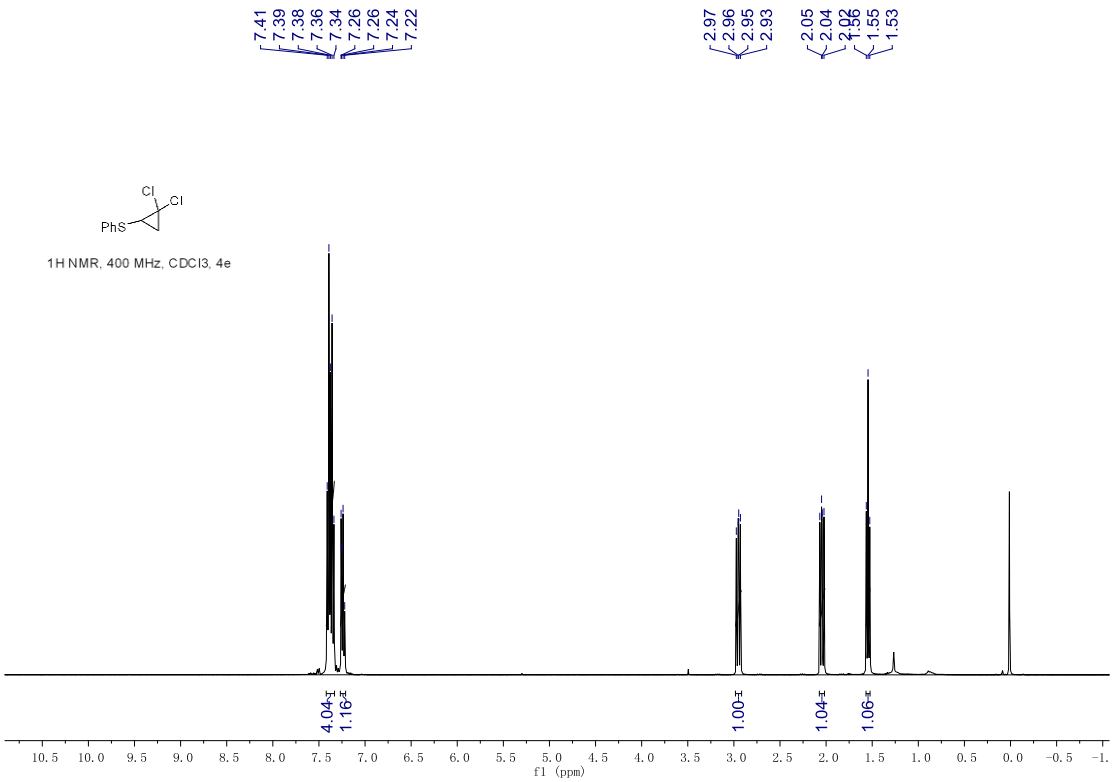


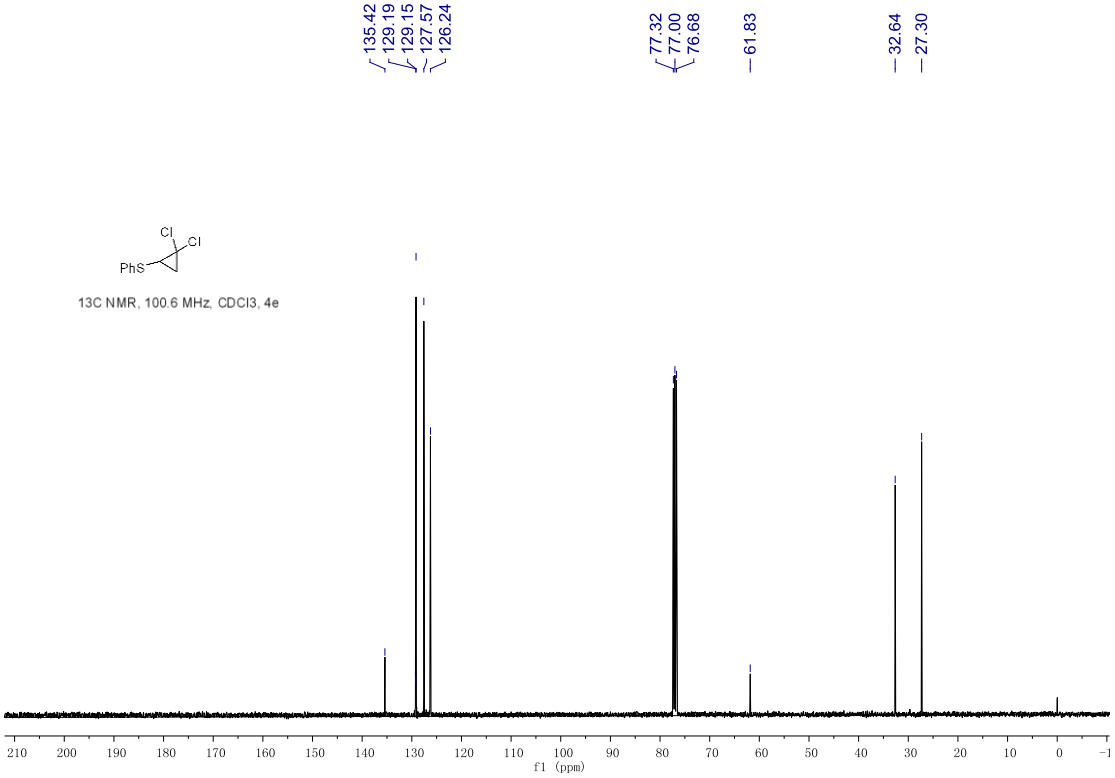
7,7-dichlorobicyclo[4.1.0]heptane 4d:



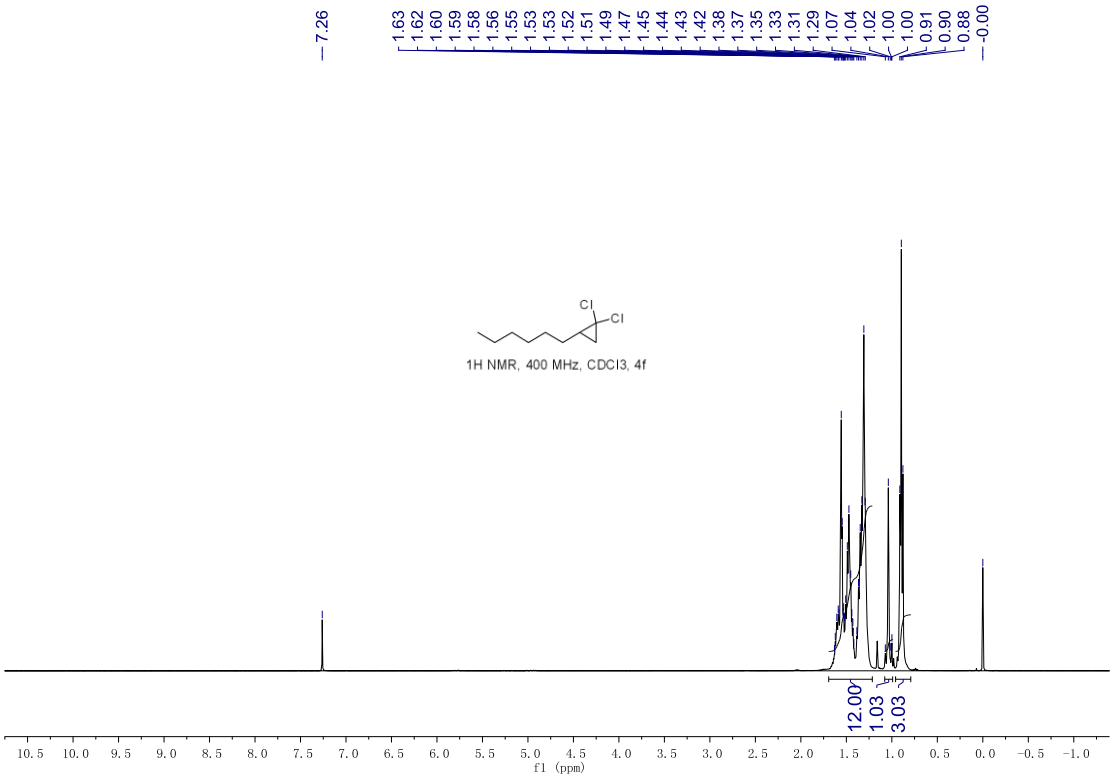


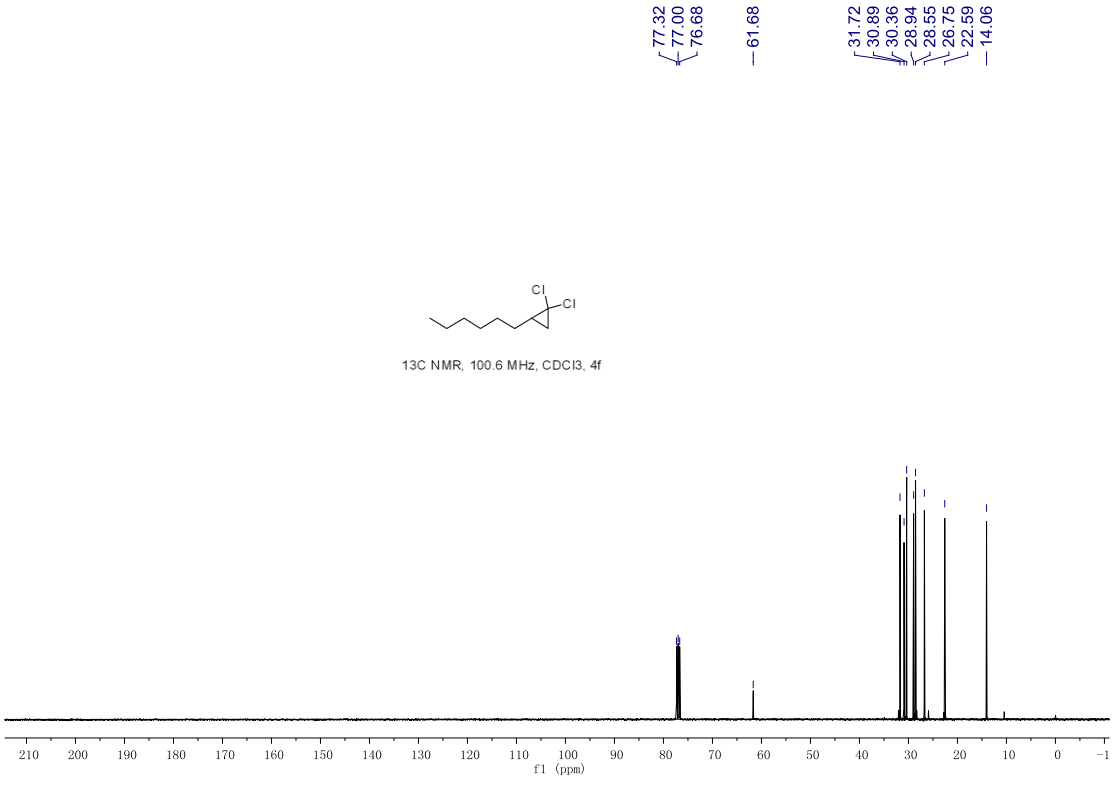
(2,2-dichlorocyclopropyl)-phenylsulfane 4e:



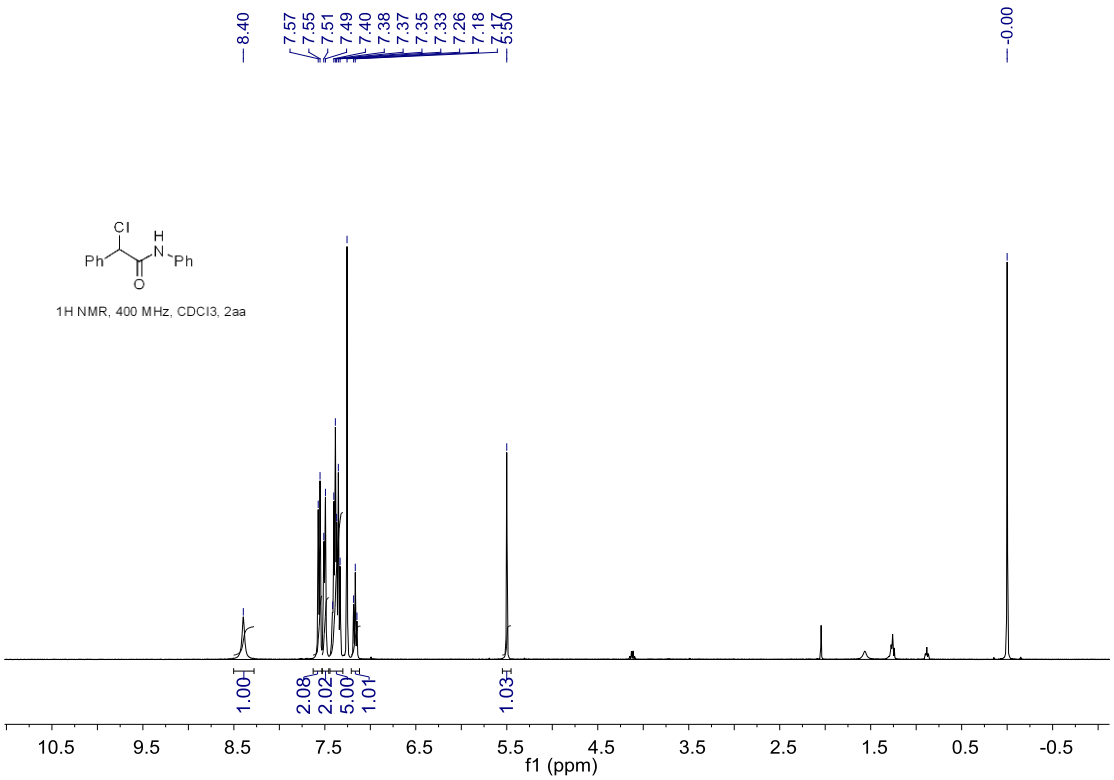


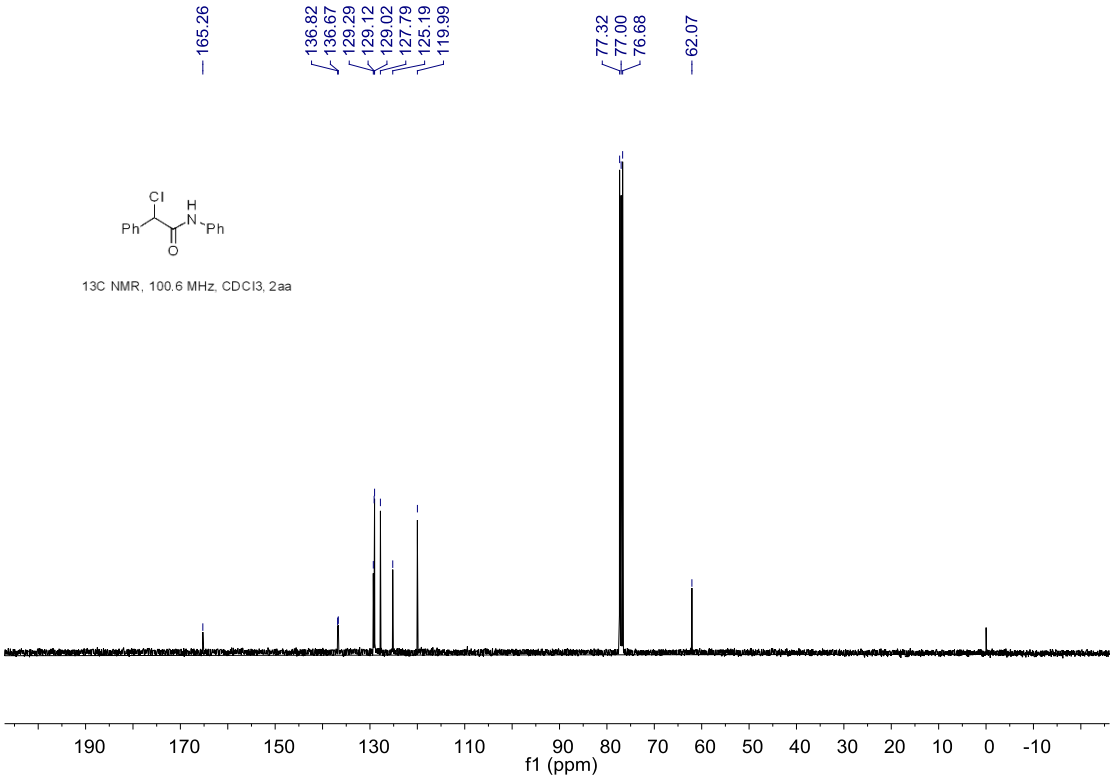
1,1-dichloro-2-hexylcyclopropane 4f:



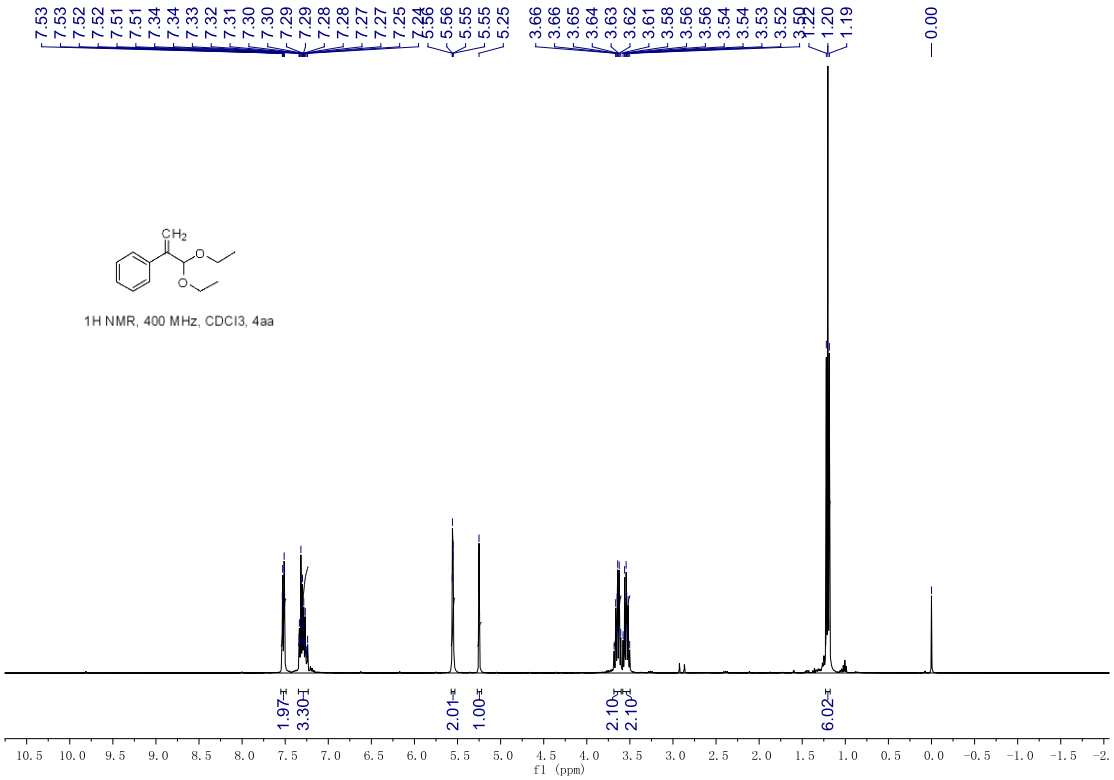


The charts of ^{1}H and ^{13}C NMR of N-phenyl-*α*-chlorophenylacetamide 2aa.





The charts of ^{1}H and ^{13}C NMR of (3,3-diethoxyprop-1-en-2-yl)benzene 4aa.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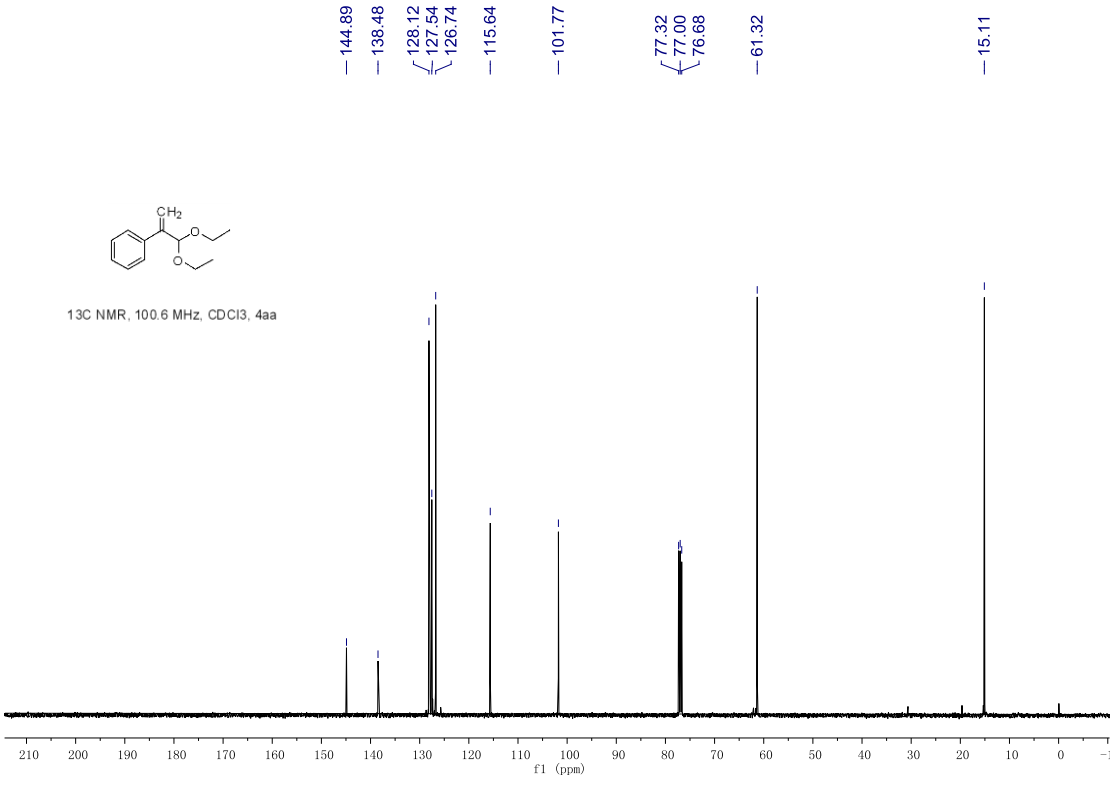
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CH2
O
O
13C NMR, 100.6 MHz, CDCl3, 4aa
f1 (ppm)