

A Novel Ambiphilic Dichlorocarbenoid Equivalent in Alkene-Cyclopropanation and Carbonyl-Olefination

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Supporting Information

S1	List of Contents:
S2	General Information General procedure (Method A) for the cyclopropanation of alkenes and Spectral data for 1a and 2a
S3	General procedure (Method B) for the cyclopropanation of alkenes and Spectral data for 3a, 4a, and 5a,b
S4	General procedure (Method C) for the cyclopropanation of alkenes and Spectral data for 6a,b and 7a
S5	Procedure and Spectral data for 7b, 8a,b, General procedure (Method D) for the dichloromethylenation of carbonyl compounds and Spectral data for 11a
S6	General procedure (Method E) for the dichloromethylenation of carbonyl compounds and Spectral data for 12a-15a
S7	Procedure and Spectral data for 16a-19a
S8	Procedure and Spectral data for 20a-22a
S-9-48	Copies of ^1H and ^{13}C NMR spectra for 1a, 3a, 4a, 5a,b, 6a,b, 7b, 8a,b, 11a, 12a, 13a, 15a, 17a, 18a, 19a, 20a, 21a, 22a

General Information. Dichloromethane was distilled from P₂O₅ prior to use. Commercially available ketones, and aldehydes were used as received. Titanium tetrachloride and magnesium powder (ca 50 mesh) were used as received. Substrates **19**,¹ **20**,² and **22**³ were prepared according to the reported procedures. Flash chromatography was performed on silica gel 60 (230-400 mesh). All reactions were carried out under an atmosphere of N₂. ¹H and ¹³C NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. High-resolution mass spectra were determined on a spectrometer.

¹Ito, S.; Matsumoto, M. *J. Org. Chem.* **1983**, *48*, 1133.

¹Bakuzis, P.; Bakuzis, M. L. F. *J. Org. Chem.* **1981**, *46*, 235.

³Fray, G. I.; Robinson, R. *J. Am. Chem. Soc.* **1961**, *83*, 29.

General procedure for the cyclopropanation of alkenes:

Method A: To a 0 °C suspension consisting of Mg (240 mg, 10 mmol), TiCl₄ (188 mg, 0.11 mL, 1 mmol), cyclohexene **1** (0.82 g, 1 mL, 10 mmol), CCl₄ (1.54 g, 1 mL, 10 mmol), and ClCH₂CH₂Cl (15 mL) was added THF (0.5 mL). After being stirred for 1-2 h at 0 °C, a solution of saturated potassium carbonate solution (10 mL) was added and the mixture was diluted with ether (30 mL). The organic layer was separated, dried, evaporated, and purified by chromatography on silica gel (elution with hexane) to give **7,7-dichlorobicyclo[4.1.0]heptane 1a** (1.58 g, 95% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 1.95-1.90 (m, 2 H), 1.68-1.61 (m, 4 H), 1.32-1.26 (m, 2 H), 1.21-1.15 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 68.0, 25.8, 20.2, 18.8; high-resolution MS m/e Calcd for C₇H₁₀Cl₂: 164.0160. Found: 164.0155. Its spectral properties were in agreement with literature values, see: (a) Ishihara, T.; Ando, T.; Muranaka, T.; Saito, K. *J. Org. Chem.* **1977**, *42*, 666. (b) Perlikowska, W.; Modro, A. M.; Modro, T. A.; Mphahlele, M. J. *J. Chem. Soc., Perkin Trans. 2.* **1996**, *12*, 2611.

6,6-Dichlorobicyclo[3.1.0]hexane 2a: Following the procedure of method A, 0.68 g (10 mmol) of **2** and Mg (240 mg, 10 mmol)/TiCl₄ (188 mg, 0.11 mL, 1 mmol)/CCl₄ (1 mL, 10 mmol)/ClCH₂CH₂Cl (15 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by distillation afforded 1.2 g (81%) of **2a** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 2.08-2.05 (m, 2 H), 2.03-1.91 (m, 4 H), 1.64-1.59 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 68.2, 38.1, 27.7, 25.1; high-resolution MS m/e Calcd for C₆H₈Cl₂: 150.0003. Found: 150.0011. Anal. Calcd for C₆H₈Cl₂: C, 47.71; H, 5.34. Found: C, 47.49; H, 5.42. Its spectral properties were in agreement with literature values, see: (a) Kidemet, D.; Mihalic,

Z.; Novak, I.; Vancik, H. *J. Org. Chem.* **1999**, *64*, 4931. (b) Bergman, E. *J. Org. Chem.* **1963**, *28*, 2210. (c) Jayachandran, J. P.; Wang, M.-L. *Synth. Commun.* **1999**, *29*, 4101.

Method B: To a 0 °C suspension consisting of Mg (240 mg, 10 mmol), styrene **3** (1.04 g, 10 mmol), CCl₄ (1.54 g, 10 mmol), THF (0.5 mL), and ClCH₂CH₂Cl (15 mL) was added TiCl₄ (188 mg, 0.11 mL, 1 mmol). After being stirred for 1 h at 0 °C, a solution of saturated potassium carbonate solution (10 mL) was added and the mixture was diluted with ether (30 mL). The organic layer was separated, dried, evaporated, and purified by chromatography on silica gel (elution with hexane) to give **1,1-dichloro-2-phenylcyclopropane 3a** (1.68 g, 90% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.25 (m, 5 H), 2.92 (dd, *J* = 10.4, 8.4 Hz, 1 H), 2.00 (dd, *J* = 10.4, 8.4 Hz, 1 H), 1.87 (t, *J* = 8.4 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 134.6, 128.9, 128.3, 127.6, 60.7, 35.4, 25.6. Its spectral properties were in agreement with literature values, see: (a) Regen, S. L.; Singh, A. *J. Org. Chem.* **1982**, *47*, 1587. (b) Jayachandran, J. P.; Wang, M.-L. *Synth. Commun.* **1999**, *29*, 4101.

1,1-Dichloro-trans-2,3-diphenylcyclopropane 4a: Following the procedure of method B, 180 mg (1 mmol) of **4** and Mg (192 mg, 8 mmol)/TiCl₄ (94 mg, 0.06 mL, 0.5 mmol)/CCl₄ (1 mL, 10 mmol)/ClCH₂CH₂Cl (3 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) and crystallization afforded 218 mg (83%) of **4a** as a white solid: mp 39-40 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.14 (m, 10 H), 3.15 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 134.8, 129.2, 128.7, 128.1, 65.6, 40.0. Its spectral properties were in agreement with literature values, see: Seyferth, D.; Minasz, R. J.; Treiber, A. J.-H.; Burlitch, J. M.; Dowd, S. R. *J. Org. Chem.* **1963**, *28*, 1163.

7,7-Dichlorobicyclo[4.1.0]hept-3-ene 5a: Following the procedure of method A, 0.8 g (10 mmol) of **5** and Mg (0.24 g, 10 mmol)/TiCl₄ (0.11 mL, 1 mmol)/CCl₄ (1 mL, 10 mmol)/ClCH₂CH₂Cl (15 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 1.44 g (90%) of **5a** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 5.49 (bs, 2 H), 2.45-2.39 (m, 2 H), 2.18-2.14 (m, 2 H), 1.79-1.77 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 122.4, 66.0, 23.9, 19.0. Its spectral properties were in agreement with literature values, see: (a) Okazaki, R.; O-oka, M.; Tokitoh, N.; Inamoto, N. *J. Org. Chem.* **1985**, *50*, 180. (b) Billups, W. E.; Blakeney, A. J.; Chow, W. Y. *Org. Synth.* **1976**, *55*, 12.

anti-4,4,8,8-Tetrachlorotricyclo[5.1.0.0^{3,5}]octane 5b: Following the procedure of method A, 0.16 g (1 mmol) of **5a** and Mg (3 mmol)/TiCl₄ (0.3 mmol)/CCl₄ (5 mmol)/ClCH₂CH₂Cl (3 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) and crystallization (ether and ethyl acetate) afforded 2.25 g (94%) of **5b** as a white solid: mp 169-170 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.12-2.10 (m, 4 H), 1.62-1.60 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 63.6, 23.2, 12.1. Its spectral properties were

in agreement with literature values, see: (a) Kuhn, W.; Marschall, H.; Weyerstahl, P. *Chem. Ber.* **1977**, *110*, 1564. (b) Fieser, L. F.; Sachs, D. H. *J. Org. Chem.* **1964**, *29*, 1113.

9,9-Dichlorobicyclo[6.1.0]non-4-ene 6a: Following the procedure of method A, 0.11 g (1 mmol) of **6** and Mg (3 mmol)/TiCl₄ (0.3 mmol)/CCl₄ (5 mmol)/ClCH₂CH₂Cl (3 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 0.18 g (92%) of **6a** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 5.55 (dd, *J* = 5.2, 3.2 Hz, 2 H), 2.38-2.31 (m, 2 H), 2.14-2.02 (m, 4 H), 1.88-1.81 (m, 2 H), 1.65-1.61 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 129.1, 66.3, 32.2, 25.9, 24.5. Its spectral properties were in agreement with literature values, see: Hanold, N.; Meier, H. *Chem. Ber.* **1985**, *118*, 198.

syn-5,5,10,10-Tetrachlorotricyclo[7.1.0.0^{4,6}]decane 6b: Following the procedure of method A, 0.19 g (1 mmol) of **2** and Mg (144 mg, 6 mmol)/TiCl₄ (94 mg, 0.06 mL, 0.5 mmol)/CCl₄ (5 mmol)/ClCH₂CH₂Cl (3 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) and crystallization (ether and ethyl acetate) afforded 0.23 g (85%) of **6b** as a white solid: mp 176-177 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.17-2.14 (m, 4 H), 1.71-1.70 (m, 4 H), 1.60-1.54 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 65.9, 31.0, 21.3. Its spectral properties were in agreement with literature values, see: (a) Fieser, L. F.; Sachs, D. H. *J. Org. Chem.* **1964**, *29*, 1113. (b) Hanold, N.; Meier, H. *Chem. Ber.* **1985**, *118*, 198. (c) Kuhn, W.; Marschall, H.; Weyerstahl, P. *Chem. Ber.* **1977**, *110*, 1564.

Method C: To a 0 °C suspension consisting of Mg (144 mg, 6 mmol), TiCl₄ (94 mg, 0.06 mL, 0.5 mmol), CCl₄ (1.54 g, 10 mmol), and ClCH₂CH₂Cl (3 mL) was added THF (0.3 mL) dropwise, during which time a pale black color developed. After being stirred for 1-2 min at 0 °C, a solution of bicyclobutene **7** (134 mg, 1 mmol) in ClCH₂CH₂Cl (1 mL) was added. The black mixture was stirred for an additional 1 h, treated with a solution of saturated potassium carbonate solution (4 mL), and diluted with ether (10 mL). The organic layer was separated, dried, evaporated, and purified by chromatography on silica gel (elution with hexane) to give **11,11-dichlorotricyclo[4.4.1]undec-3-ene 7a** (182 mg, 84% yield): ¹H NMR (400 MHz, CDCl₃) δ 5.50 (bs, 2 H), 2.48 (d, *J* = 16.4 Hz, 2 H), 2.18 (d, *J* = 16.4 Hz, 2 H), 1.92-1.29 (m, 8 H); ¹³C NMR (100 MHz, CDCl₃) δ 123.5, 65.9, 30.4, 29.6, 26.1, 20.0; high-resolution MS *m/e* Calcd for C₁₁H₁₄Cl₂: 216.0472. Found: 216.0466. Anal. Calcd for C₁₁H₁₄Cl₂: C, 60.84; H, 6.50. Found: C, 60.51; H, 6.44. Its spectral properties were in agreement with literature values, see: Seyferth, D.; Minas, R. J.; Treiber, A. J.-H.; Burlitch, J. M.; Dowd, S. R. *J. Org. Chem.* **1963**, *28*, 1163..

anti-4,4,12,12-Tetrachlorotetracyclo[5.4.1.0^{1,7}.0^{3,5}]dodecane 7b: Following the procedure of method C, 217 mg (1 mmol) of **7a** and Mg (288 mg, 12 mmol)/TiCl₄ (0.7

mmol)/CCl₄ (1 mL, 10 mmol)/ClCH₂CH₂Cl (4 mL)/THF (0.3 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) and recrystallization afforded 258 mg (86%) of **7b** as a white solid: mp 135-136 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.45-2.38 (m, 2 H), 1.96-1.91 (m, 2 H), 1.89-1.58 (m, 6 H), 1.38-1.25 (m, 2 H), 1.23-1.19 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 73.5, 65.9, 29.7, 25.2, 25.0, 24.1, 20.7. Its spectral properties were in agreement with literature values, see: Banwell, M. G.; Ryan, J. H.; Winkler, D. A. *Aust. J. Chem.* **1991**, *44*, 593.

11,11-Dichlorotricyclo[4.4.1]undeca-3,8-diene 8a and anti-4,4,12,12-Tetrachlorotetracyclo[5.4.1.0^{1,7}.0^{3,5}]dodece-9-ne 8b: Following the procedure of method C, 132 mg (1 mmol) of **8** and Mg (144 mg, 6 mmol), TiCl₄ (94 mg, 0.06 mL, 0.5 mmol), CCl₄ (1.54 g, 10 mmol)/ClCH₂CH₂Cl (4 mL)/THF (0.3 mL) gave a 63:12 mixture of **8a** and **8b**. Purification by flash chromatography (silica gel, hexane) and recrystallization afforded. **8a** (136 mg, 63%): mp 80-82 °C ¹H NMR (400 MHz, CDCl₃) δ 5.51 (bs, 4 H), 2.53 (d, *J* = 16.8 Hz, 4 H), 2.28 (d, *J* = 16.8 Hz, 4 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 123.31, 74.24, 30.44, 24.83. **8b** (36 mg, 12%): mp 133-135 °C ¹H NMR (400 MHz, CDCl₃) δ 5.43 (bs, 2 H), 2.51-2.40 (m, 4 H), 2.20-2.15 (m, 2 H), 1.94-1.90 (m, 2 H), 1.71-1.69 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 122.8, 71.7, 64.7, 30.8, 25.0, 24.3, 23.5. Their spectral properties were in agreement with literature values, see: (a) Sims, J. J.; Honwad, V. K. *J. Org. Chem.* **1969**, *34*, 496. (b) Hashem, Md. A.; Marschall-Weyerstahl, H.; Weyerstahl, P. *Chem. Ber.* **1986**, *119*, 464.

General procedure for the dichloromethylenation of carbonyl compounds:

Method D: At 0 °C, adamantanone **11** (150 mg, 1 mmol) in CCl₄ (3 mL) and THF (1 mL) was added to a suspension consisting of Mg (192 mg, 8 mmol) and TiCl₄ (2 mmol, 1 M in CH₂Cl₂, 2 mL). After the initial exotherm had ceased, the cooling bath was removed. The black slurry was stirred for 1 h, then cooled to 0 °C, and carefully poured into ice-cold saturated potassium carbonate solution (10 mL). The resulting mixture was stirred with 20 mL of ether and the phases were separated. After this procedure was repeated twice, the combined extracts were dried, evaporated, and purified by chromatography on silica gel (elution with 100:1 hexane-ethyl acetate) to give dichloride **2-dichloromethyleneadamantane 11a** (198 mg, 92% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 3.09 (bs, 2 H), 1.93-1.71 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 107.1, 37.8, 36.4, 34.6, 27.4; high-resolution MS *m/e* Calcd for C₁₁H₁₄Cl₂: 216.0473. Found: 216.0470. Its spectral properties were in agreement with literature values, see: Teodor, P.; Francisco, S.-F.; Albert, V. *Magn. Reson. Chem.* **1997**, *35*, 30.

1-Dichloromethylene-2-methylcyclohexane 12a: Following the procedure of method D, 112 mg (1 mmol) of **12** and Mg (8 mmol)/TiCl₄ (2 mmol, 1 M in CH₂Cl₂, 2 mL)/CCl₄ (3

mL)/THF (1 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 153 mg (86%) of **12a** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 3.16-3.13 (m, 1 H), 2.77-2.72 (m, 1 H), 1.98 (dt, J = 14.4, 4.8 Hz, 1 H), 1.80-1.76 (m, 1 H), 1.59-1.48 (m, 5 H), 1.06 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 111.0, 33.3, 32.1, 27.2, 26.4, 19.9, 17.1; high-resolution MS m/e Calcd for $\text{C}_8\text{H}_{12}\text{Cl}_2$: 178.0316. Found: 178.0317. Its spectral properties were in agreement with literature values, see: Oku, A.; Harada, T.; Hattori, K.; Nazaki, Y.; Yamaura, Y. *J. Org. Chem.* **1988**, *53*, 3089.

(2,2-Dichloro-1-methylvinyl)benzene 13a: Following the procedure of method D, 120 mg (1 mmol) of **13** and Mg (8 mmol)/ TiCl_4 (2 mmol, 1 M in CH_2Cl_2 , 2 mL)/ CCl_4 (3 mL)/THF (1 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 140 mg (75%) of **13a** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.25 (m, 5 H), 2.20 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 135.7, 128.3, 127.7, 127.7, 117.0, 23.0; high-resolution MS m/e Calcd for $\text{C}_9\text{H}_8\text{Cl}_2$: 186.0003. Found: 186.0002. Its spectral properties were in agreement with literature values, see: Baverman, S.; Zafrani, Y. *Tetrahedron* **1998**, *54*, 1901.

Method E: To a 0°C suspension consisting of Mg (192 mg, 8 mmol), TiCl_4 (4 mmol, 2 M in CH_2Cl_2 , 2 mL), CCl_4 (5 mL), and β -tetralone **14** (146 mg, 1 mmol) was added THF (1 mL) dropwise. After being stirred for 1 h at 0°C , a solution of saturated potassium carbonate solution (10 mL) was added. The resulting mixture was stirred with 20 mL of ether and the phases were separated. After this procedure was repeated twice, the combined extracts were dried, evaporated, and purified by chromatography on silica gel (elution with 100: 1 hexane-ethyl acetate) to give **2-dichloromethylene-1,2,3,4-tetrahydronaphthalene 14a** (170 mg, 80% yield) as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 7.10-7.07 (m, 4H), 4.86 (d, J = 1.2 Hz, 1 H, $\text{HC}=\text{C}$), 4.83 (d, J = 1.2 Hz, 1 H, $\text{HC}=\text{C}$), 3.52 (s, 2 H, $(\text{H}_2\text{C})\text{C}=\text{C}$), 2.84 (t, J = 6.4 Hz, 2 H, $(\text{H}_2\text{C})_2\text{C}=\text{C}$), 2.46 (t, J = 6.4 Hz, 2 H, $(\text{H}_2\text{C})_2\text{C}=\text{C}$); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 137.0, 128.5, 128.3, 125.9, 125.8, 125.5, 108.2, 37.1, 31.8, 31.2; high-resolution MS m/e Calcd for $\text{C}_{11}\text{H}_{10}\text{Cl}_2$: 212.0160. Found: 212.0168. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{Cl}_2$: C, 61.99; H, 4.73. Found: C, 61.76; H, 4.65.

2-Dichloromethyleneindane 15a: Following the procedure of method E, 132 mg (1 mmol) of **15** and Mg (12 mmol)/ TiCl_4 (4 mmol, 1 M in CH_2Cl_2 , 4 mL)/ CCl_4 (3 mL)/THF (1 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 168 mg (85%) of **15a** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.22 (m, 4H), 3.78 (s, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.4, 139.1, 127.0, 124.6, 112.7, 39.5; high-resolution MS m/e Calcd for $\text{C}_{10}\text{H}_8\text{Cl}_2$: 198.0003. Found: 198.0005. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{Cl}_2$: C, 60.33; H, 4.05. Found: C, 60.15; H, 3.99.

2-(Dichloromethylene)-1,1-Dimethylcyclohexane 16a: Following the procedure of method E, 126 mg (1 mmol) of **16** and Mg (8 mmol)/TiCl₄ (2 mmol, 1 M in CH₂Cl₂, 2 mL)/CCl₄ (3 mL)/THF (0.5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 155 mg (81%) of **16a** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 2.46-2.43 (m, 2 H), 1.57-1.42 (m, 6 H), 1.28 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 105.1, 40.6, 37.8, 29.8, 27.2, 22.7, 19.5; high-resolution MS m/e Calcd for C₉H₁₄Cl₂: 192.0472. Found: 192.0466. Anal. Calcd for C₉H₁₄Cl₂: C, 55.97; H, 7.30. Found: C, 55.76; H, 7.24.

1,1-Dichloro-4-phenylbutene 17a: Following the procedure of method D, 1.34 g (10 mmol) of **17** and Mg (40 mmol)/TiCl₄ (15 mmol, 1 M in CH₂Cl₂, 15 mL)/CCl₄ (15 mL)/THF (5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 1.21 g (64%) of **17a** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.18 (m, 5 H), 5.87 (t, *J* = 7.2 Hz, 1 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 2.50 (dt, *J* = 7.6, 7.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 128.8, 128.4, 128.3, 126.2, 120.6, 34.2, 31.2; high-resolution MS m/e Calcd for C₁₀H₁₀Cl₂: 200.0159. Found: 200.0160. Its spectral properties were in agreement with literature values, see: (a) Wang, Z.; Campagna, S.; Xu, G.; Pierce, M. E.; Fortunak, J. M.; Confalone, P. N. *Tetrahedron Lett.* **2000**, *41*, 4007. (b) Kochetkov, K. A. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1975**, *24*, 1464.

1-(2,2-Dichloroethenyl)-3,4-(methylenedioxy)benzene 18a: Following the procedure of method E, 1.47 g (10 mmol) of **18** and Mg (40 mmol)/TiCl₄ (15 mmol, 1 M in CH₂Cl₂, 15 mL)/CCl₄ (15 mL)/THF (5 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 1.68 g (78%) of **18a** as a colorless oil: IR (neat) 3052, 2896, 1611, 1503, 1488, 1446, 1360, 1260 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.16-6.77 (m, 3 H), 6.73 (s, 1 H), 5.97 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 147.6, 128.1, 127.3, 123.5, 119.2, 108.3, 108.2, 101.3; high-resolution MS m/e Calcd for C₉H₆Cl₂O₂: 215.9744. Found: 215.9738. Its spectral properties were in agreement with literature values, see: Tanaka, H.; Yamashita, S.; Yamanoue, M.; Torii, S. *J. Org. Chem.* **1989**, *54*, 444.

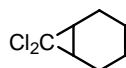
Methyl 6-(Dichloromethylene)heptanoate 19a: Following the procedure of method E, 158 mg (1 mmol) of **19** and Mg (8 mmol)/TiCl₄ (3 mmol, 1 M in ClCH₂CH₂Cl, 3 mL)/CCl₄ (1 mL)/THF (1 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 176 mg (79%) of **19a** as a colorless oil: IR (neat) 2948, 2863, 1739, 1623, 1436, 892 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.65 (s, 3 H), 2.32 (t, *J* = 7.2 Hz, 2 H), 2.25 (t, *J* = 7.2 Hz, 2 H), 1.84 (s, 3 H), 1.67-1.42 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 134.7, 114.6, 51.5, 35.0, 33.8, 26.4, 24.4, 19.7; high-resolution MS m/e

Calcd for $C_9H_{14}Cl_2O_2$: 224.0371. Found: 224.0374. Anal. Calcd for $C_9H_{14}Cl_2O_2$: C, 48.02; H, 6.26. Found: C, 48.31; H, 6.31.

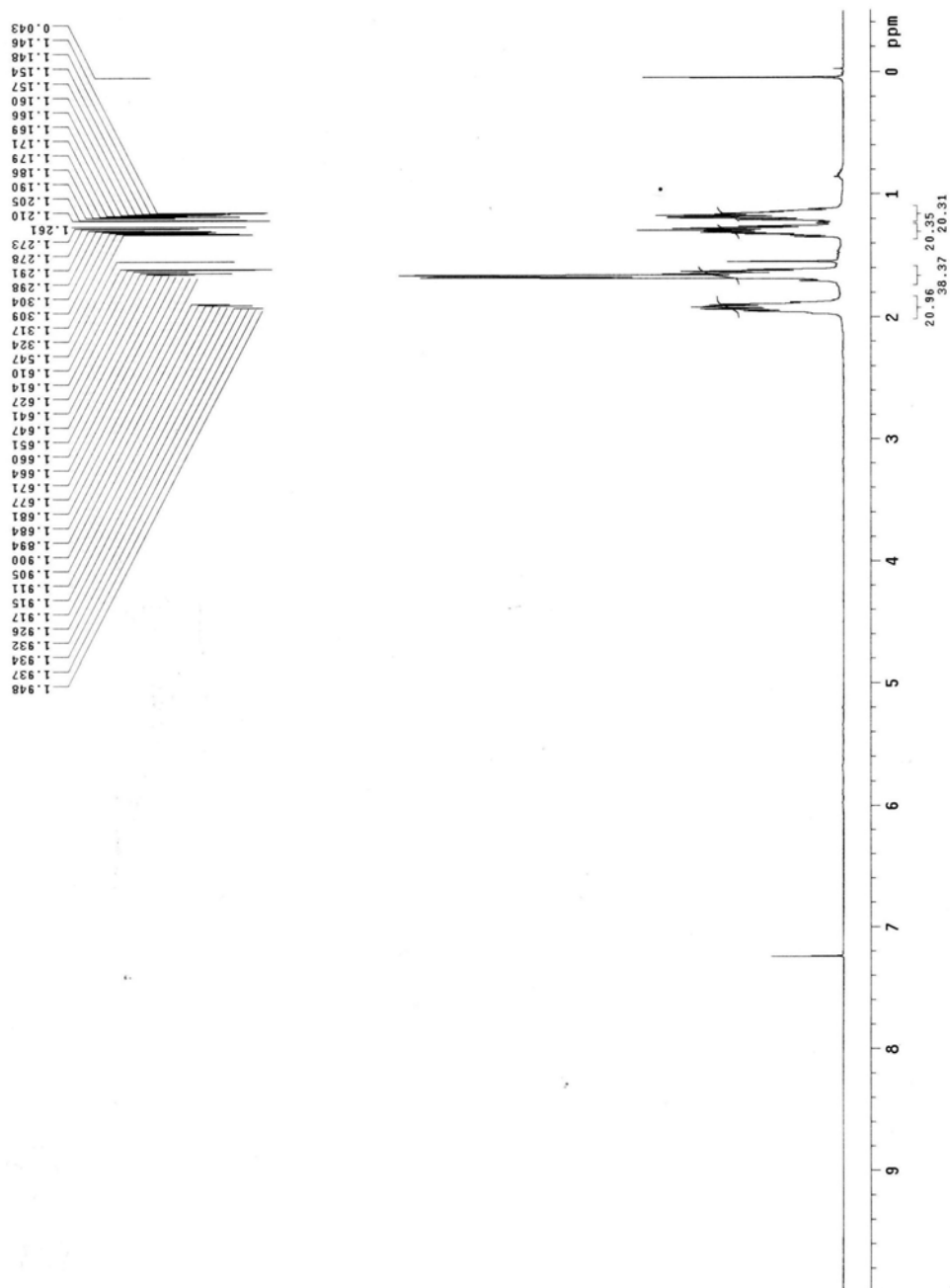
1,1-Dichloro-2-methyl-4-phenylthiobutene 20a: Following the procedure of method E, 180 mg (1 mmol) of **20** and Mg (12 mmol)/TiCl₄ (3 mmol, 1 M in CH₂Cl₂, 3 mL)/CCl₄ (4 mL)/THF (1 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 186 mg (76%) of **20a** as a colorless oil: IR (neat) 3058, 2925, 2854, 1622, 1584, 1480, 1438, 1234 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.18 (m, 5 H), 2.99 (t, *J* = 8.0 Hz, 2 H), 2.54 (t, *J* = 8.0 Hz, 2 H), 1.86 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 135.7, 133.0, 129.5, 128.9, 126.2, 116.3, 35.3, 30.8, 20.0; high-resolution MS *m/e* Calcd for C₁₁H₁₂Cl₂S: 246.0037. Found: 246.0044. Anal. Calcd for C₁₁H₁₂Cl₂S: C, 53.45; H, 4.89. Found: C, 53.55; H, 4.80.

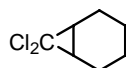
(3E)-1,1-Dichloro-2-methyl-4-phenyl-1,3-butadiene 21a: Following the procedure of method D, 146 mg (1 mmol) of **21** and Mg (8 mmol)/TiCl₄ (2 mmol, 1 M in CH₂Cl₂, 2 mL)/CCl₄ (4 mL)/THF (1 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 1.21 g (74%) of **21a** as a colorless oil: IR (neat) 3061, 3043, 2894, 1621, 1510, 1494, 1452, 1361 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.24 (m with dq at 7.26, *J* = 16, 0.8 Hz, 6 H, HC=C, ring protons), 6.68 (d, *J* = 16 Hz, 1 H, C=CH), 2.19 (d, *J* = 0.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 136.8, 131.8, 128.7, 128.6, 128.2, 126.8, 125.2, 105.1, 16.2; high-resolution MS *m/e* Calcd for C₁₁H₁₀Cl₂: 212.0159. Found: 212.0152. Anal. Calcd for C₁₁H₁₀Cl₂: C, 61.99; H, 4.73. Found: C, 61.83; H, 4.68.

1,1-Dichloro-2-(4-cyclohexenyl)propene 22a: Following the procedure of method E, 124 mg (1 mmol) of **22** and Mg (8 mmol)/TiCl₄ (1 mmol, 0.7 M in CH₂Cl₂, 1.5 mL)/CCl₄ (1 mL)/THF (0.3 mL) gave a crude reaction mixture. Purification by flash chromatography (silica gel, hexane) afforded 117 mg (62%) of **22a** as a colorless oil: IR (neat) 3025, 2930, 2838, 1652, 1612, 1435, 890 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.67 (bs, 2 H), 3.03-2.95 (m, 1 H), 2.12-2.09 (m, 2 H), 1.96-1.94 (m, 2 H), 1.77 (s, 3 H), 1.61-1.55 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 126.8, 126.0, 113.9, 38.8, 28.1, 26.3, 25.4, 15.5; high-resolution MS *m/e* Calcd for C₉H₁₂Cl₂: 190.0316. Found: 190.0318. Anal. Calcd for C₉H₁₂Cl₂: C, 56.56; H, 6.33. Found: C, 56.40; H, 6.37.

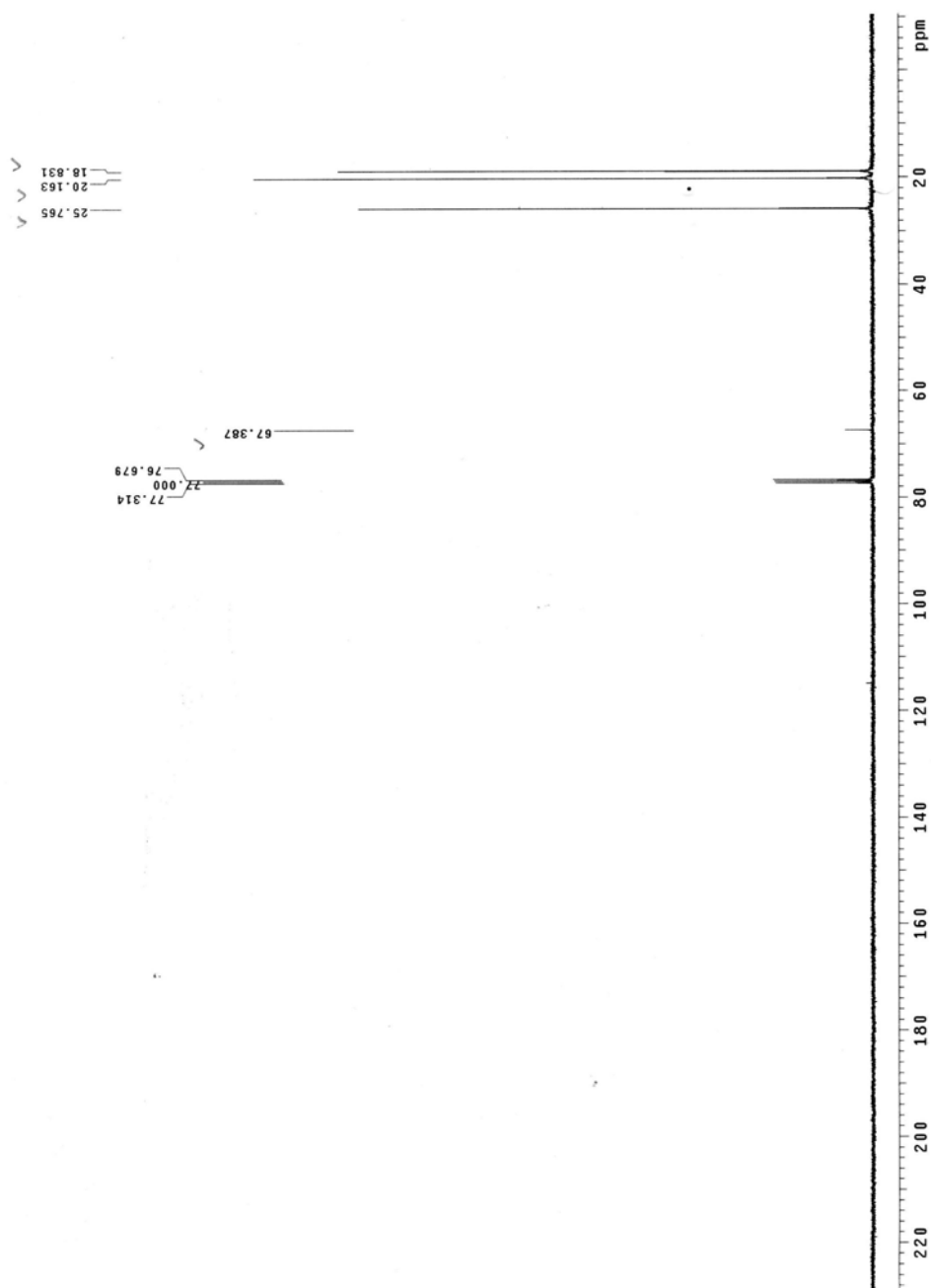


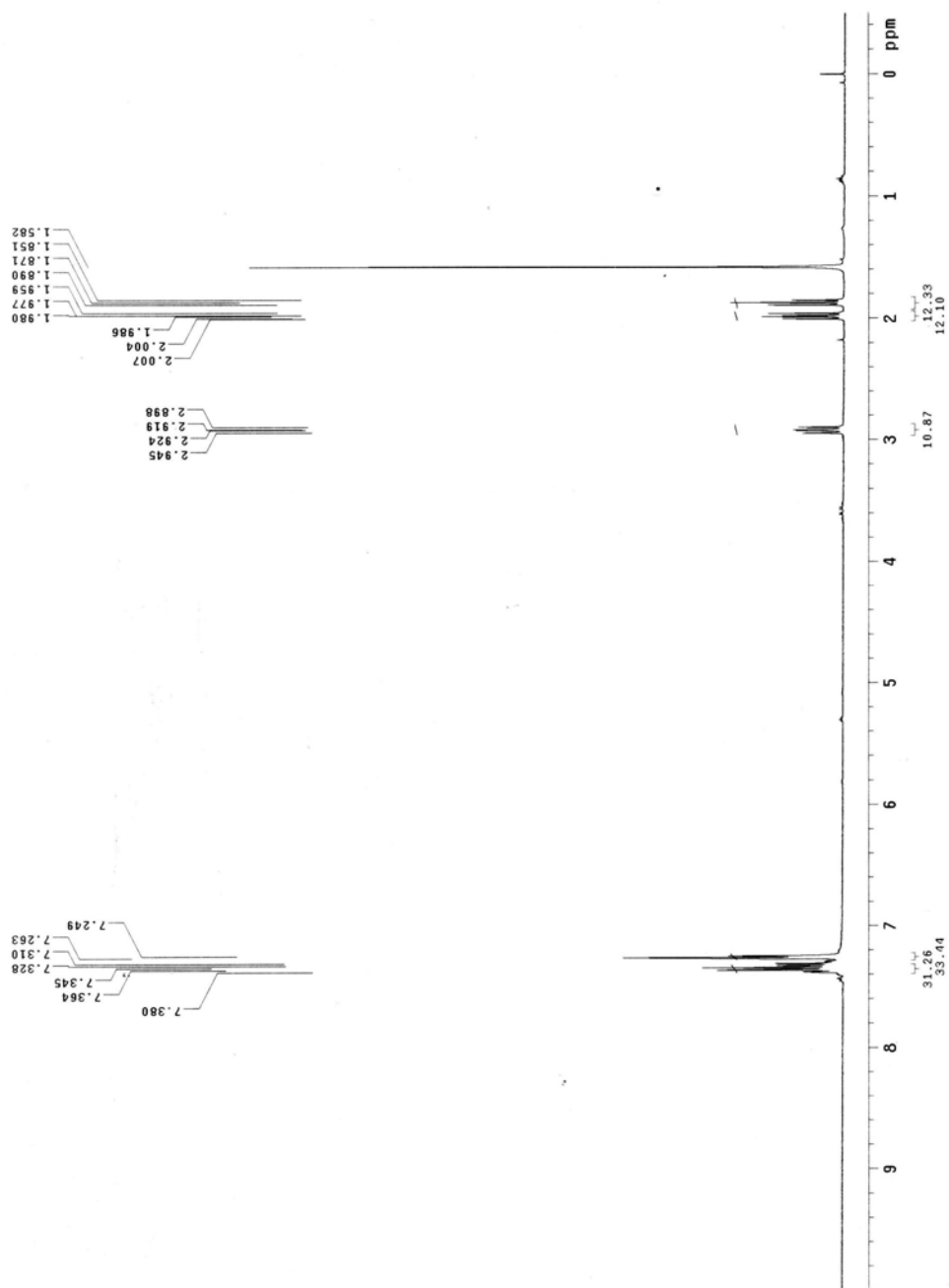
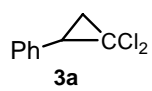
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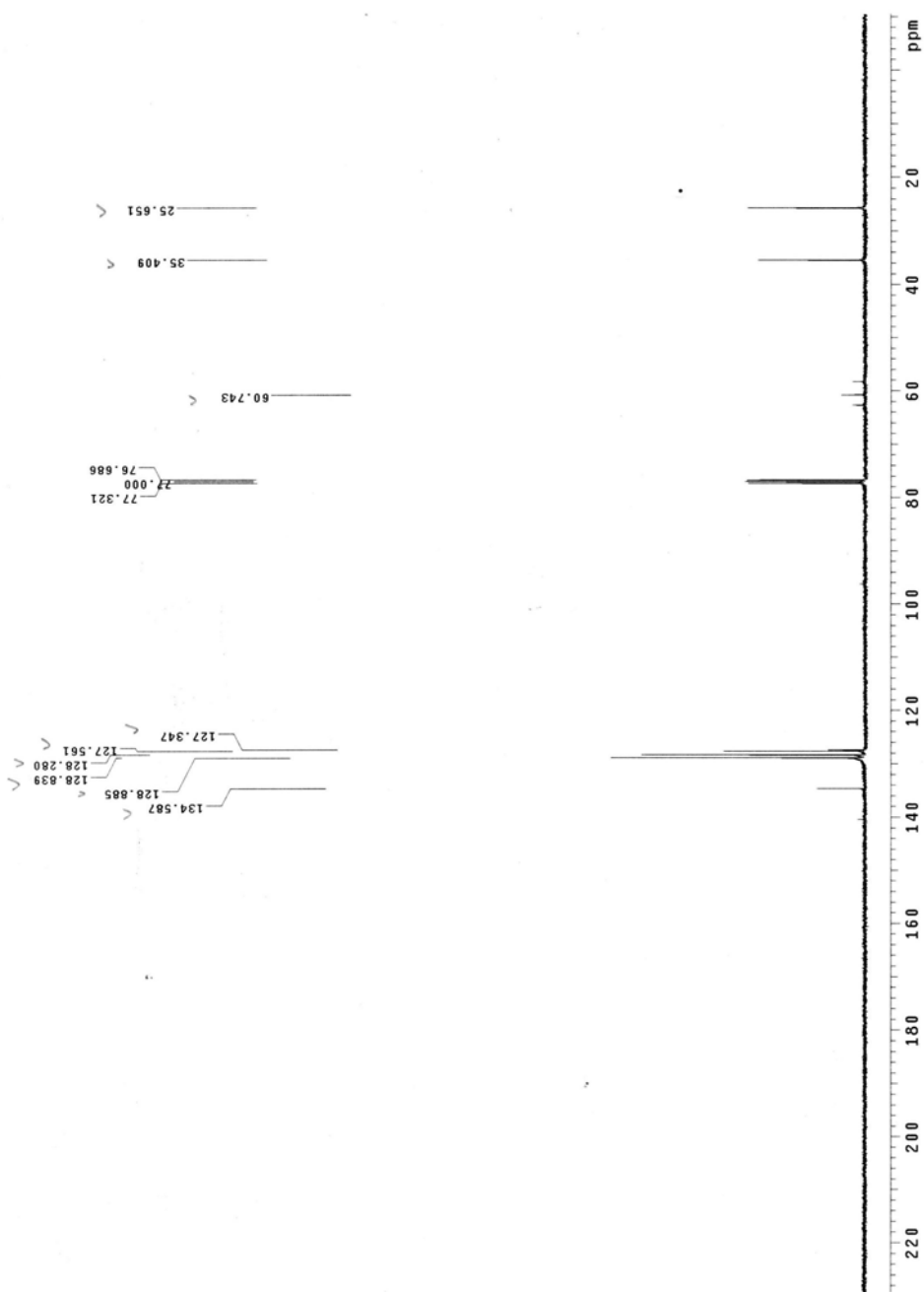
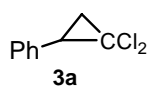


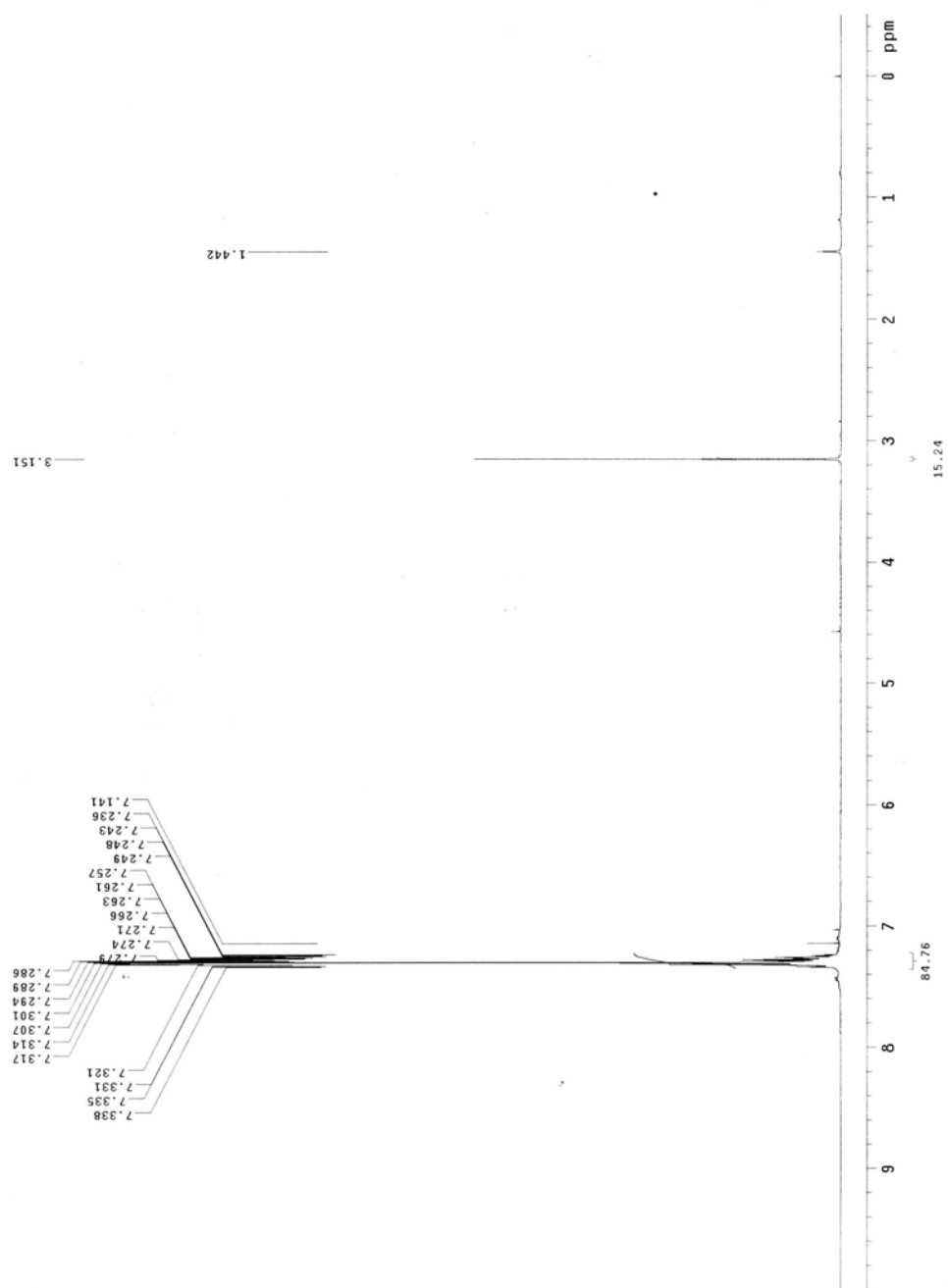
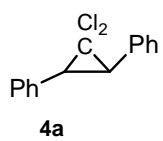


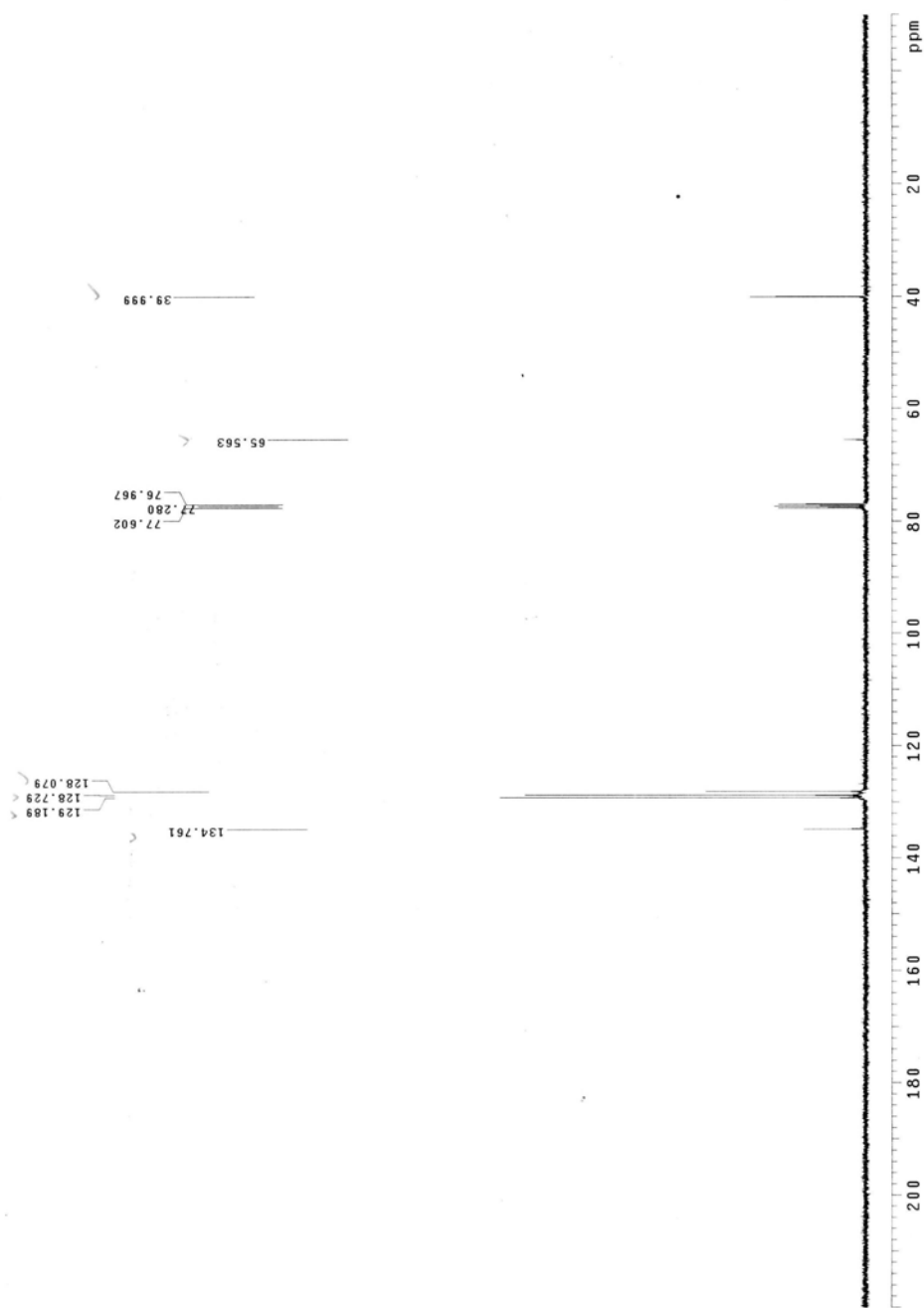
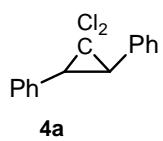
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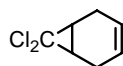




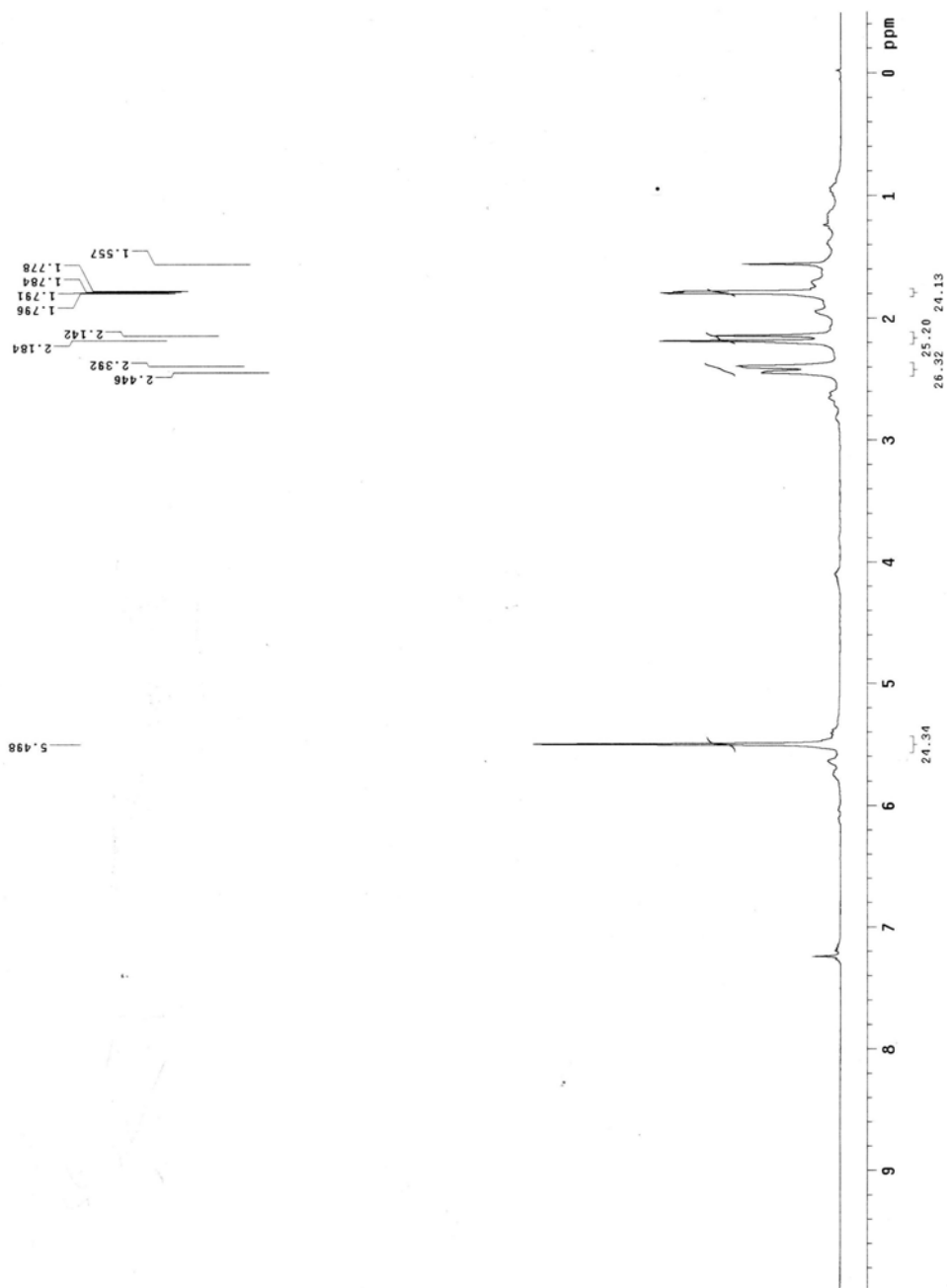


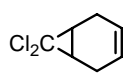




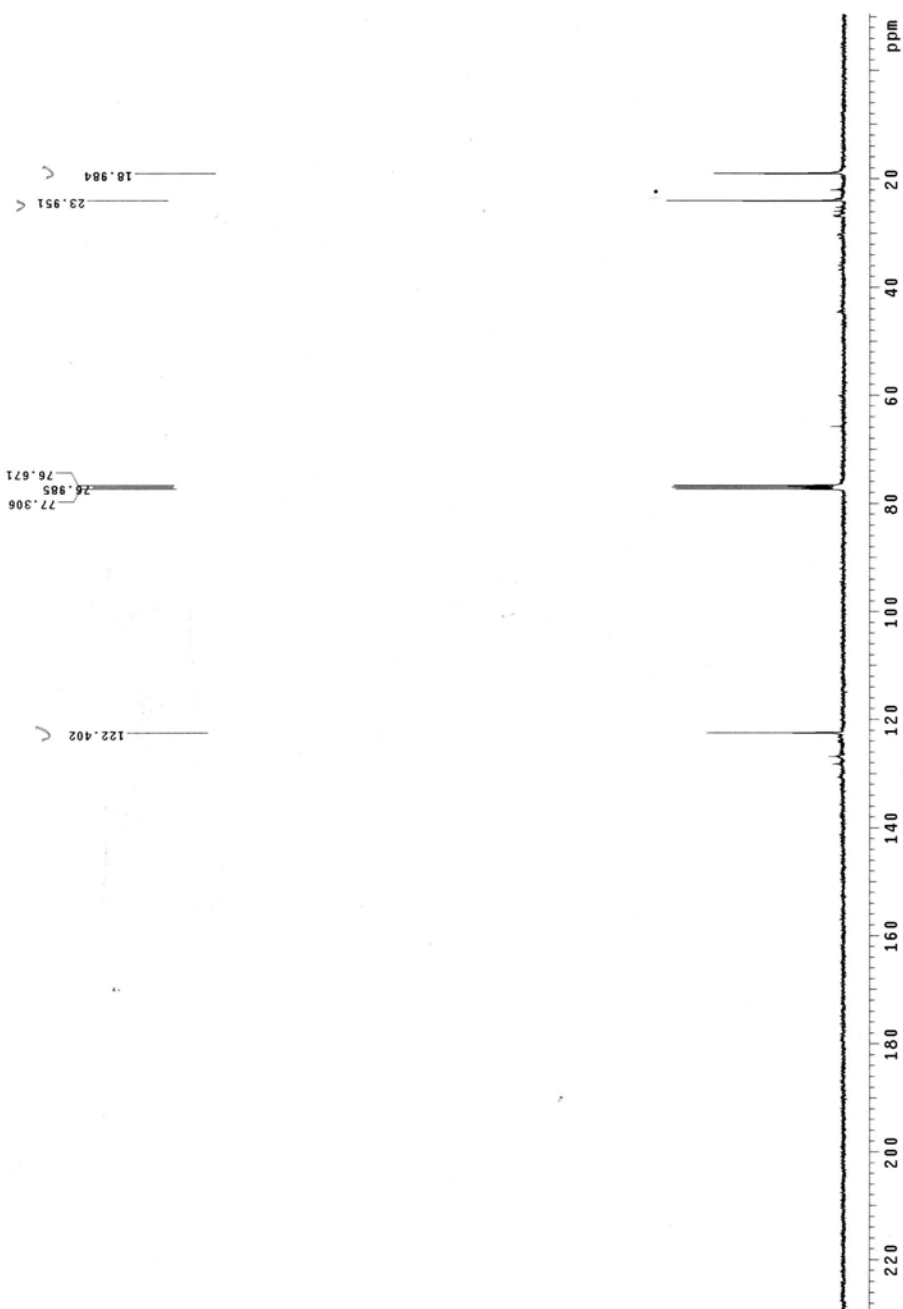


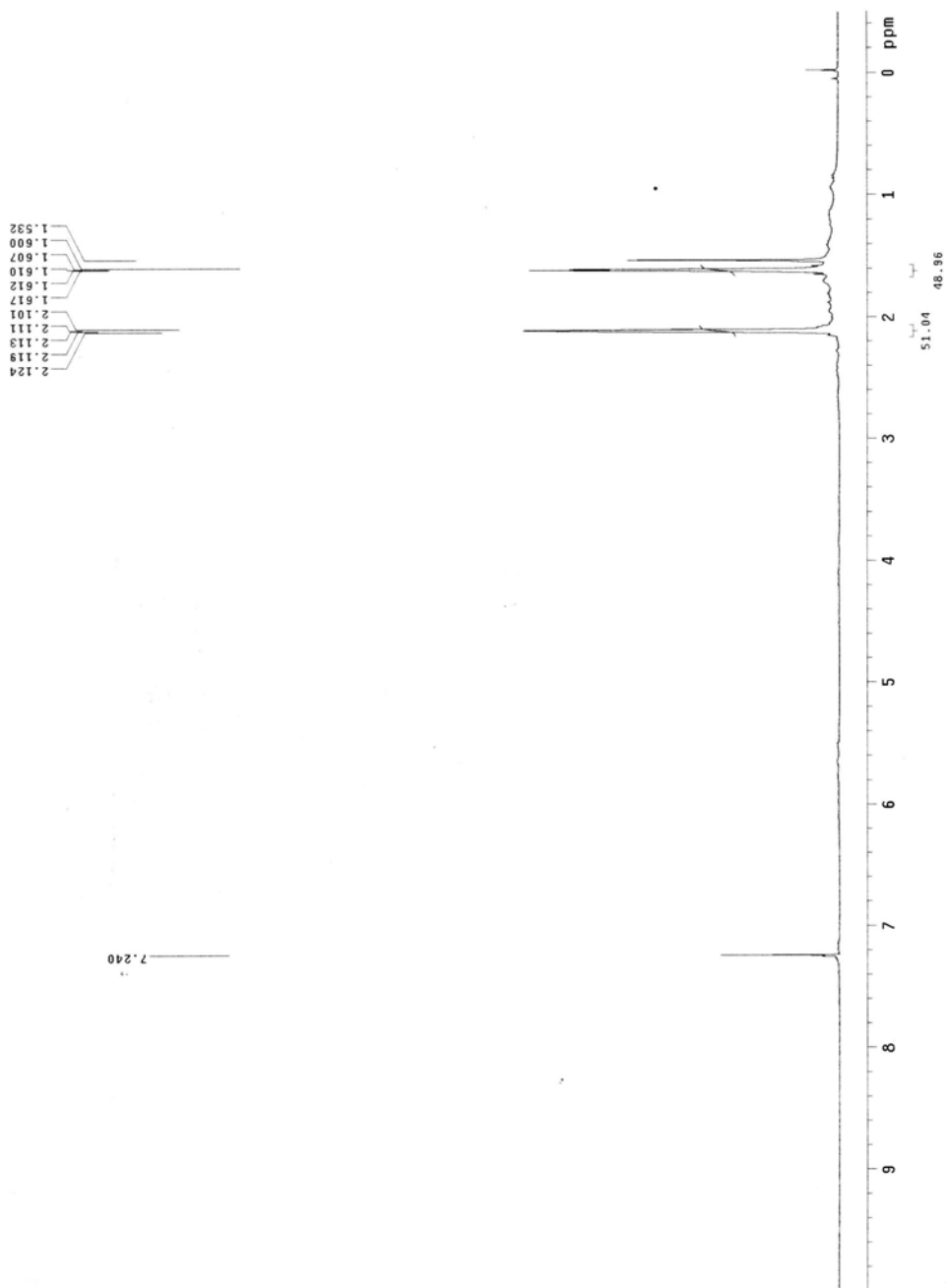
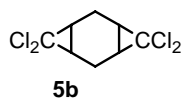
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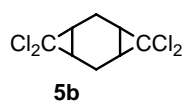
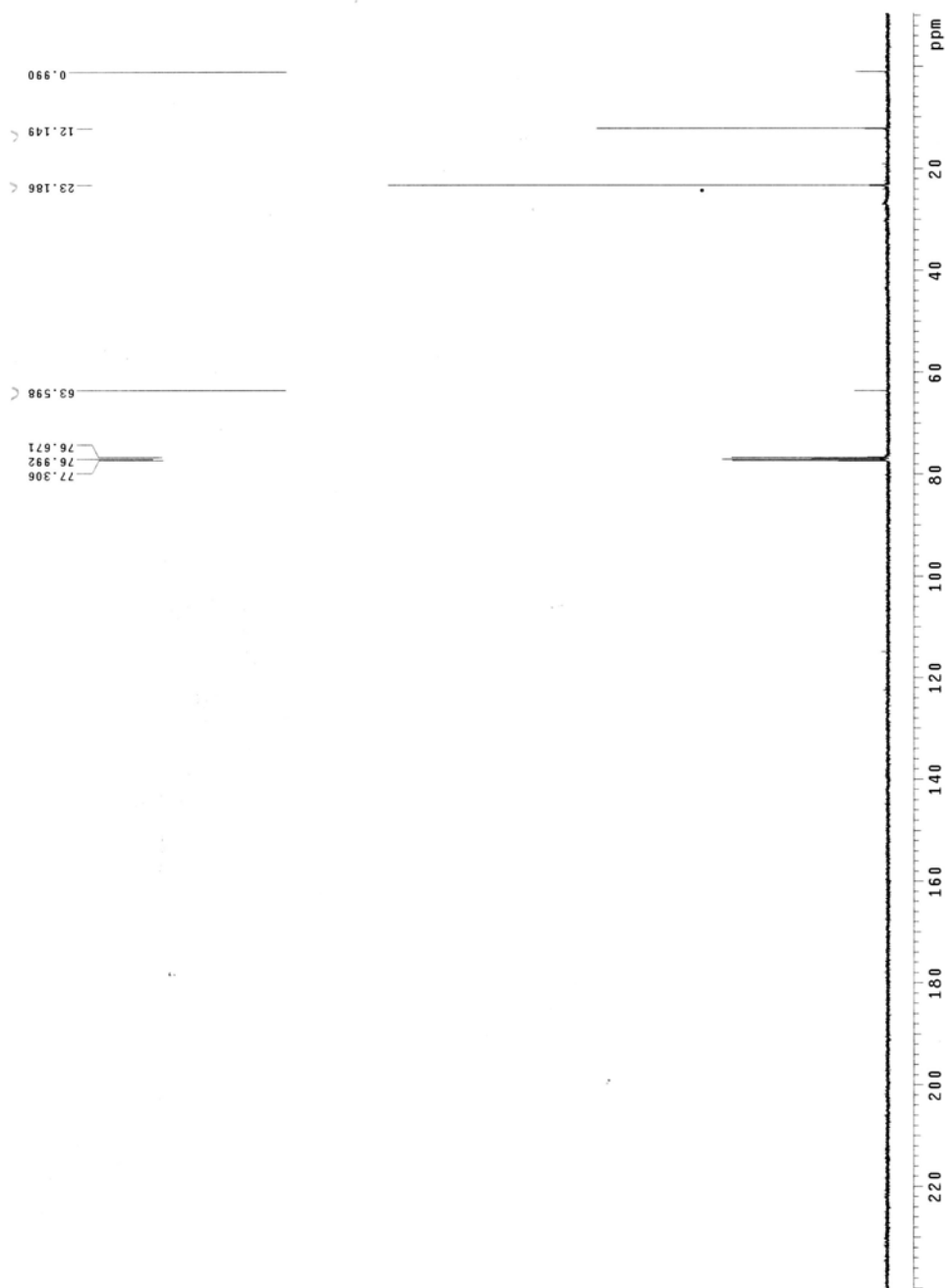


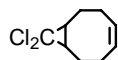


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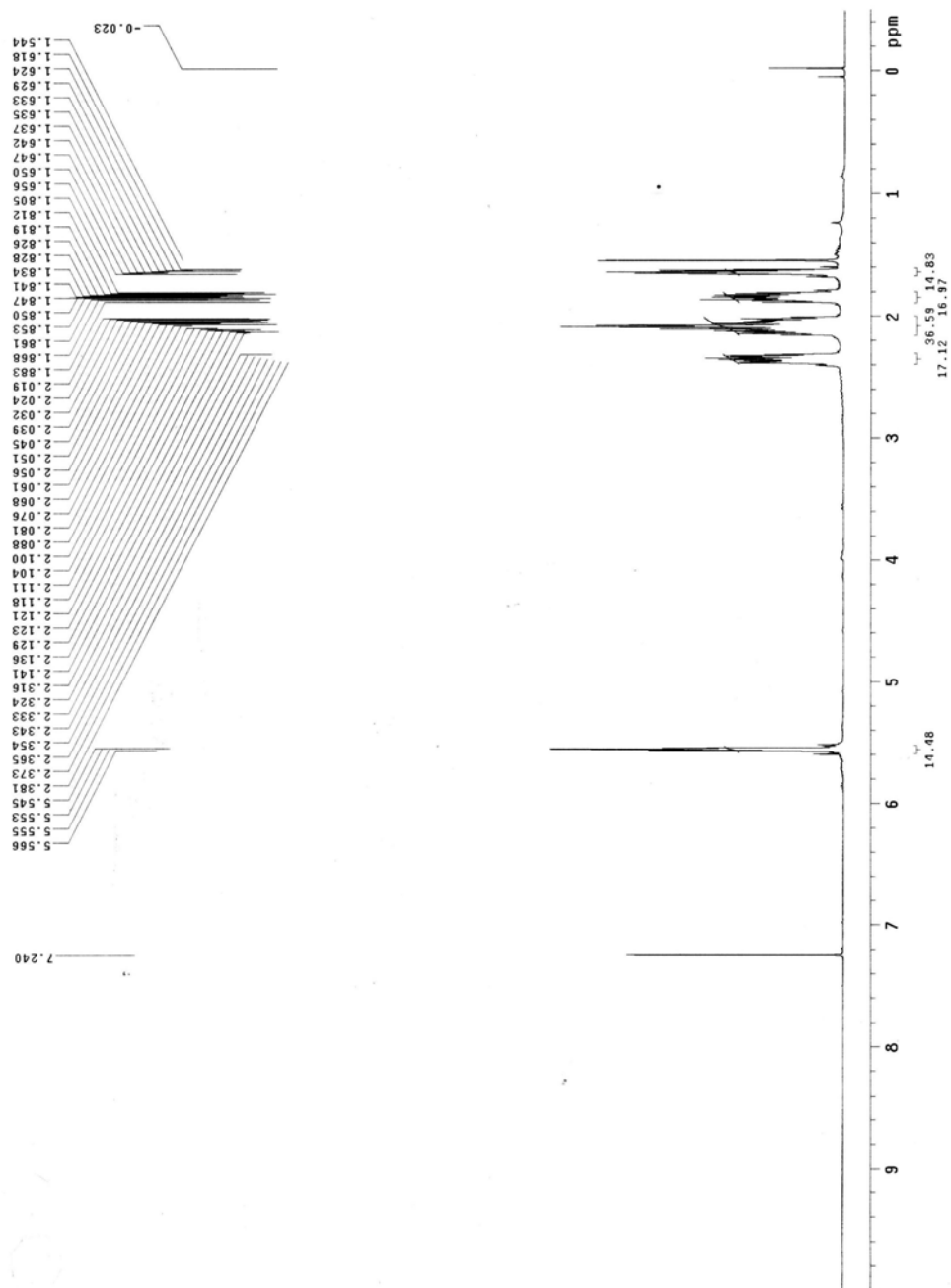


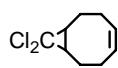




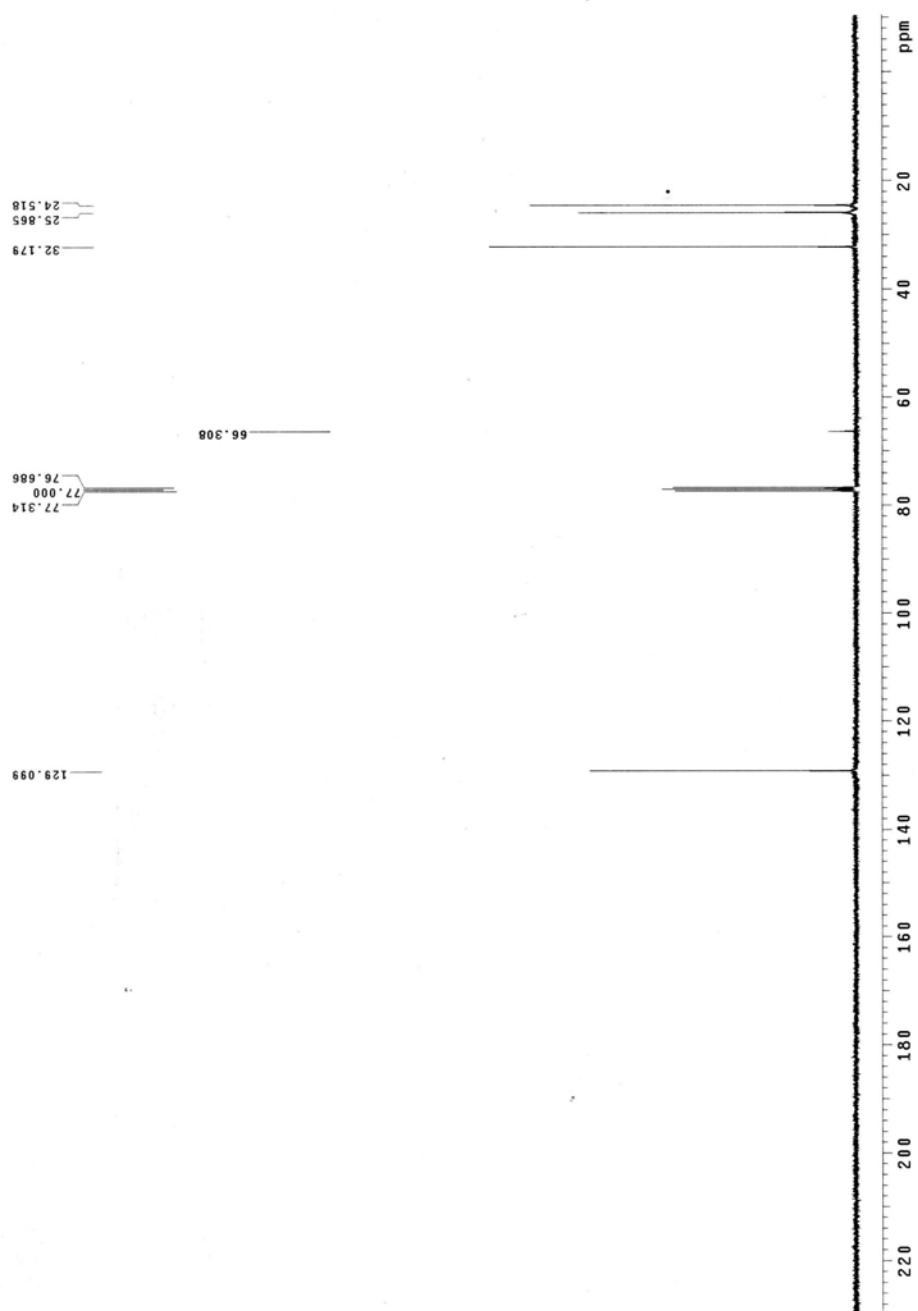


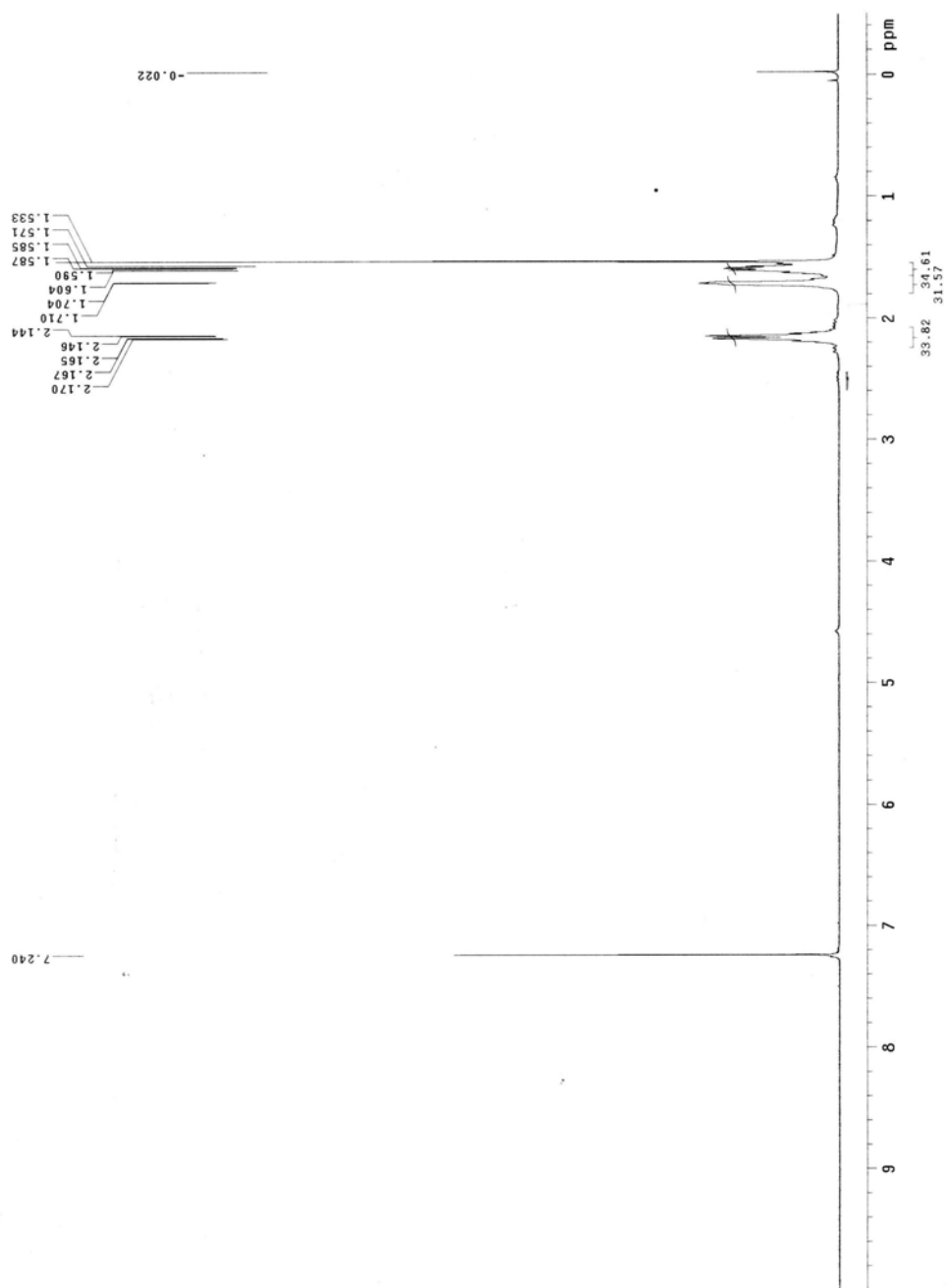
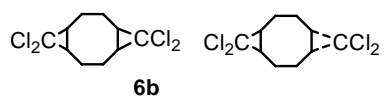
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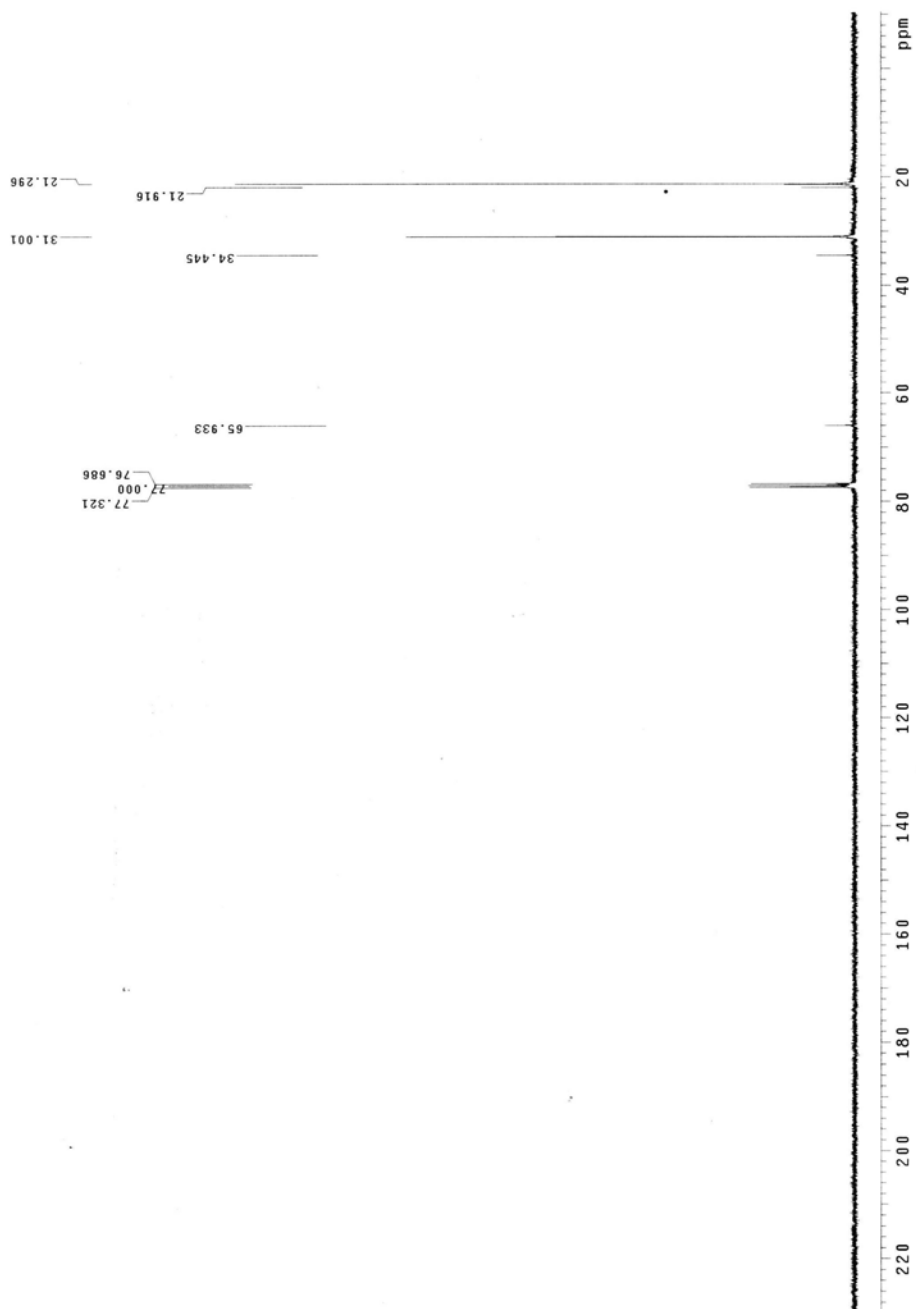
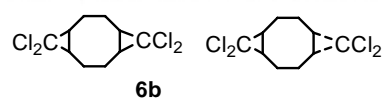


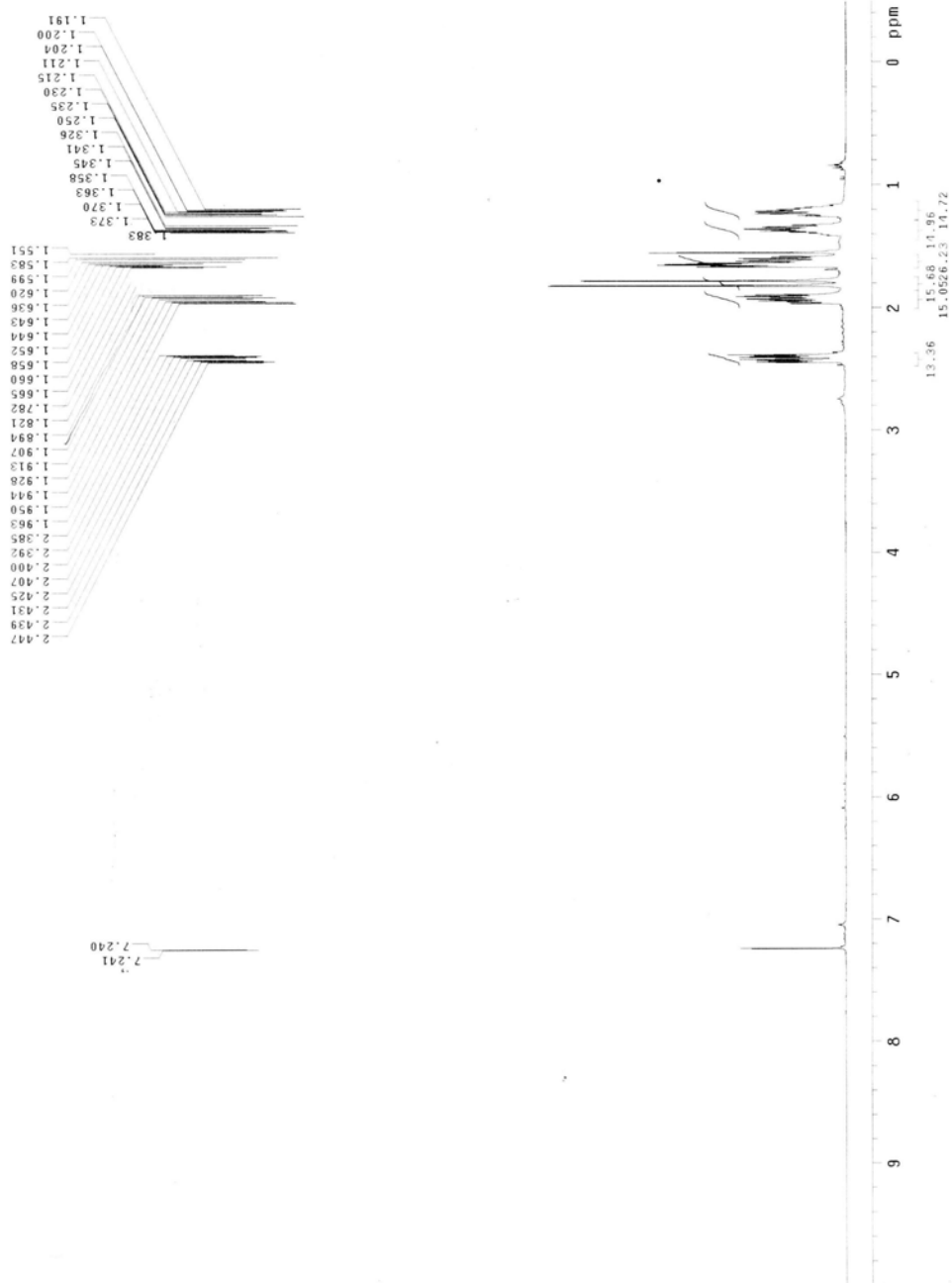
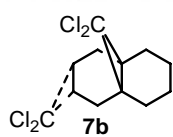


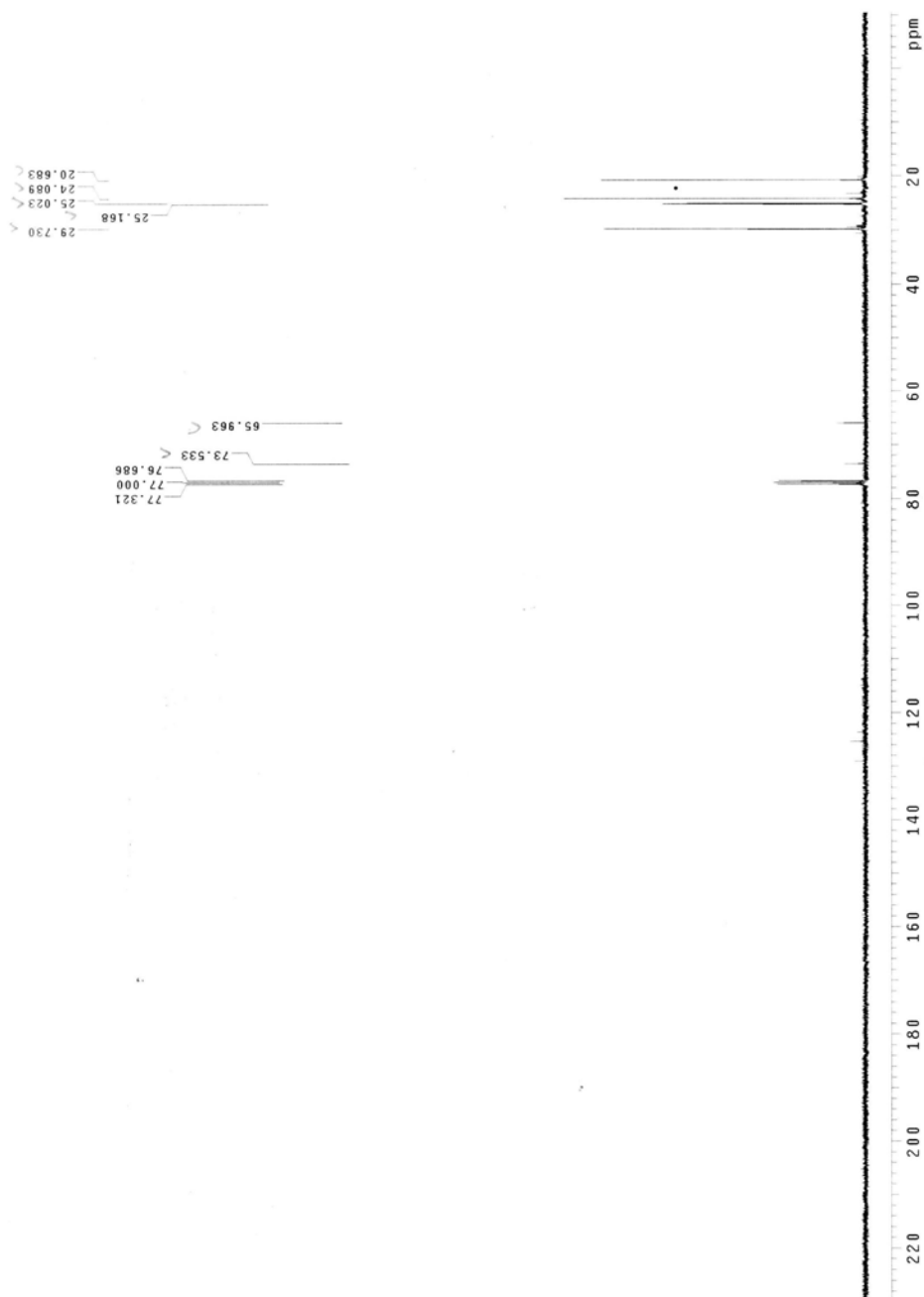
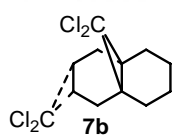
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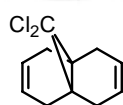




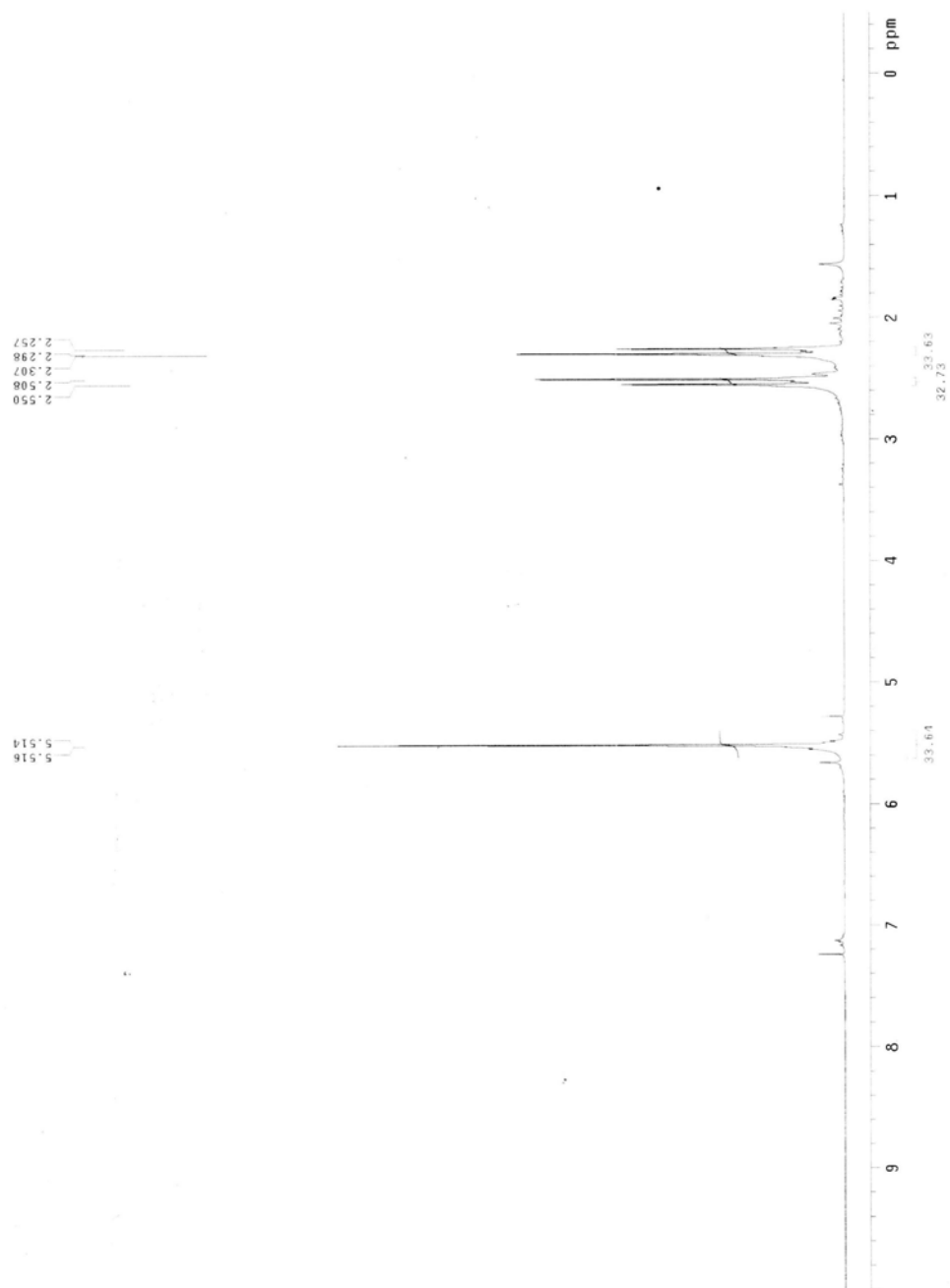


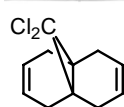




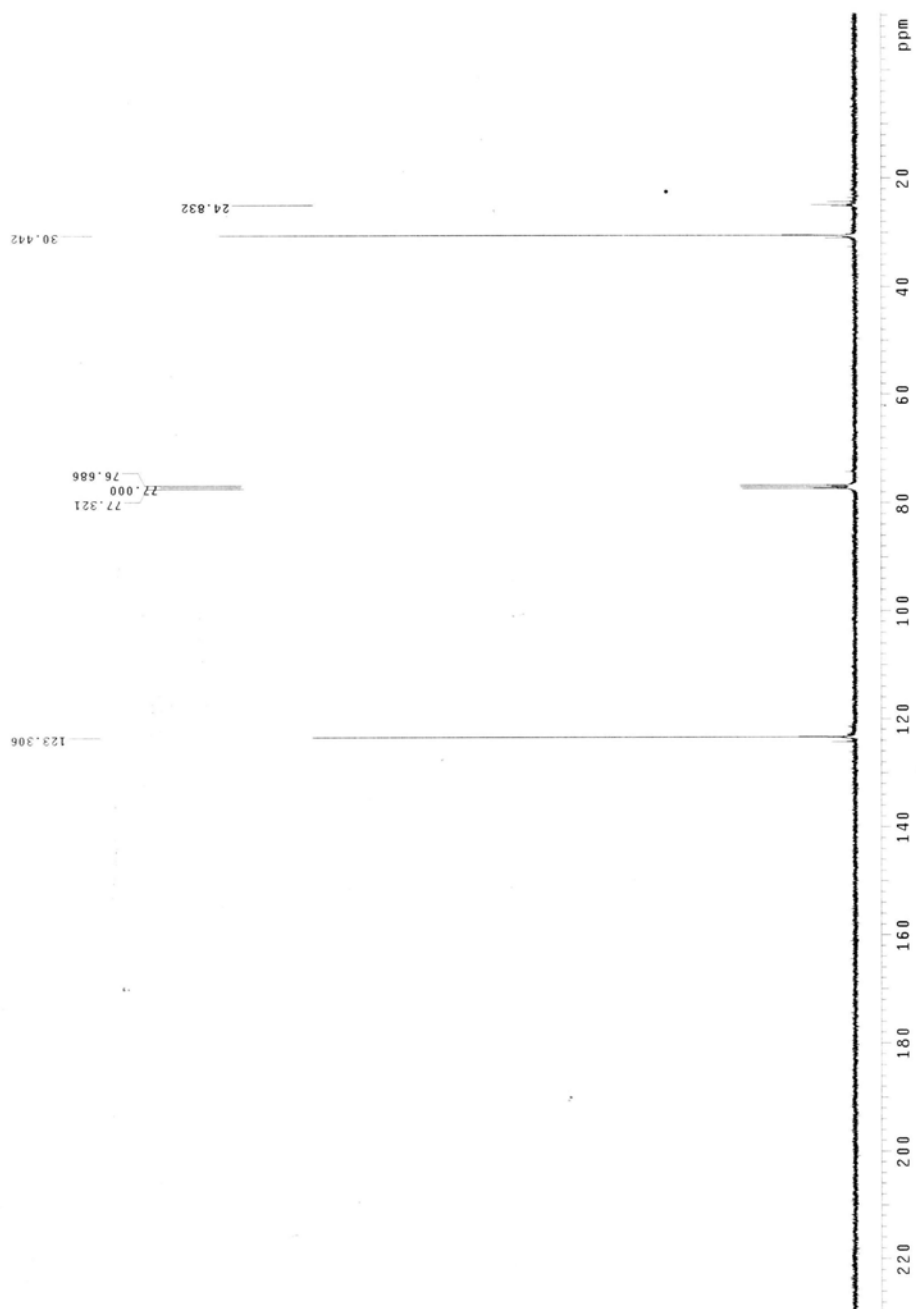


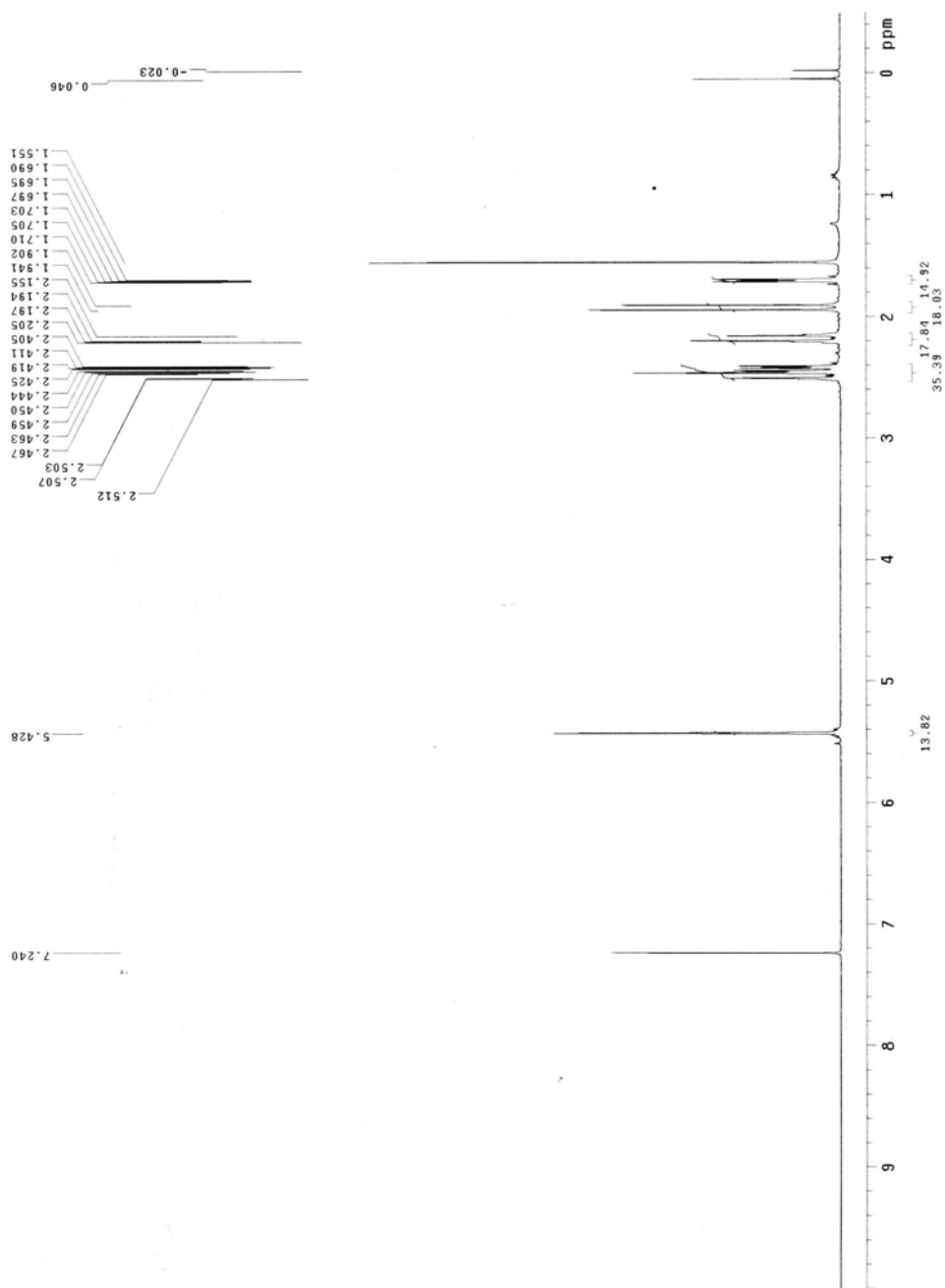
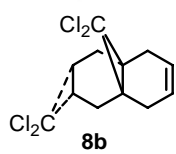
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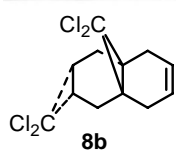
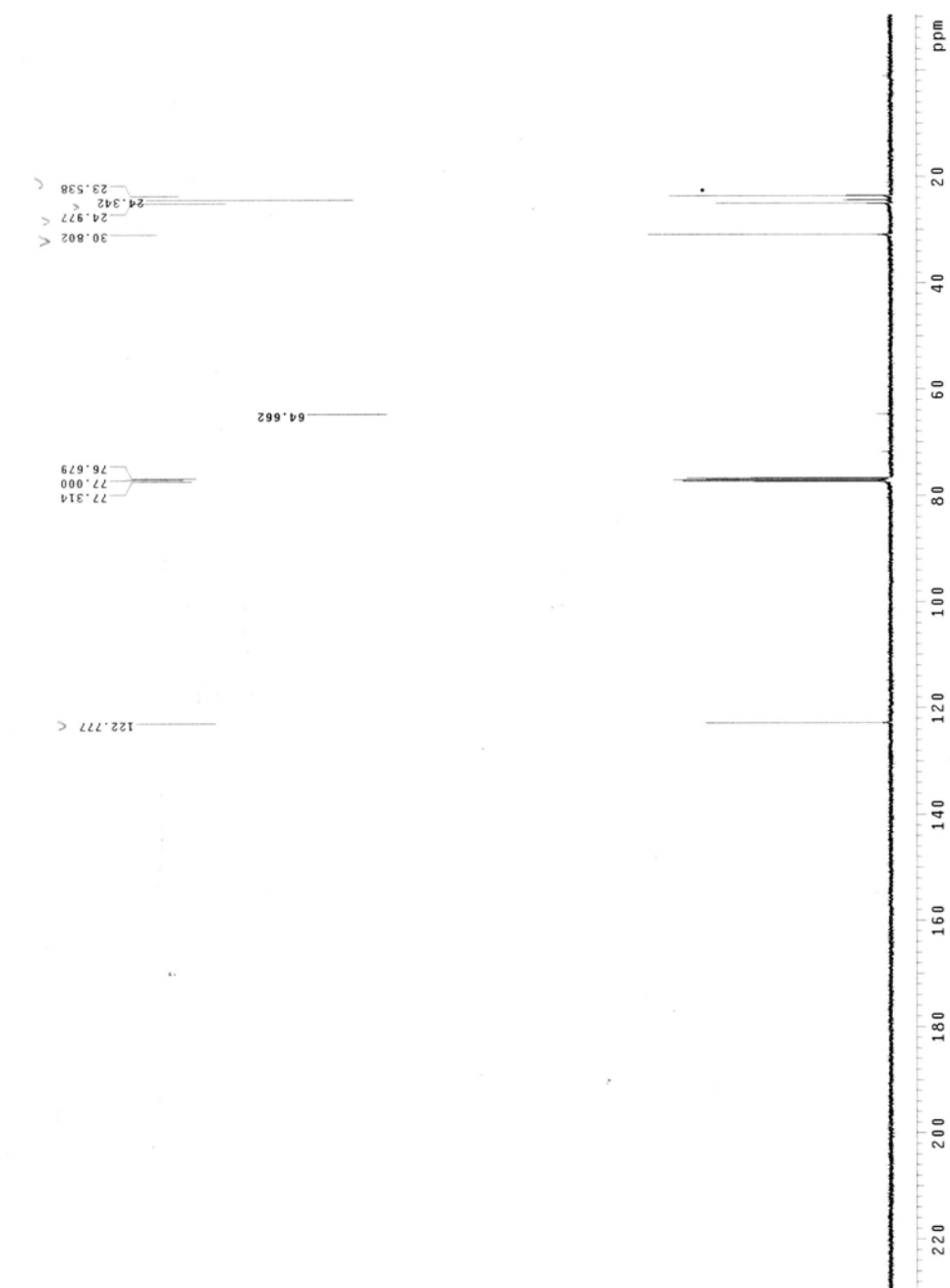


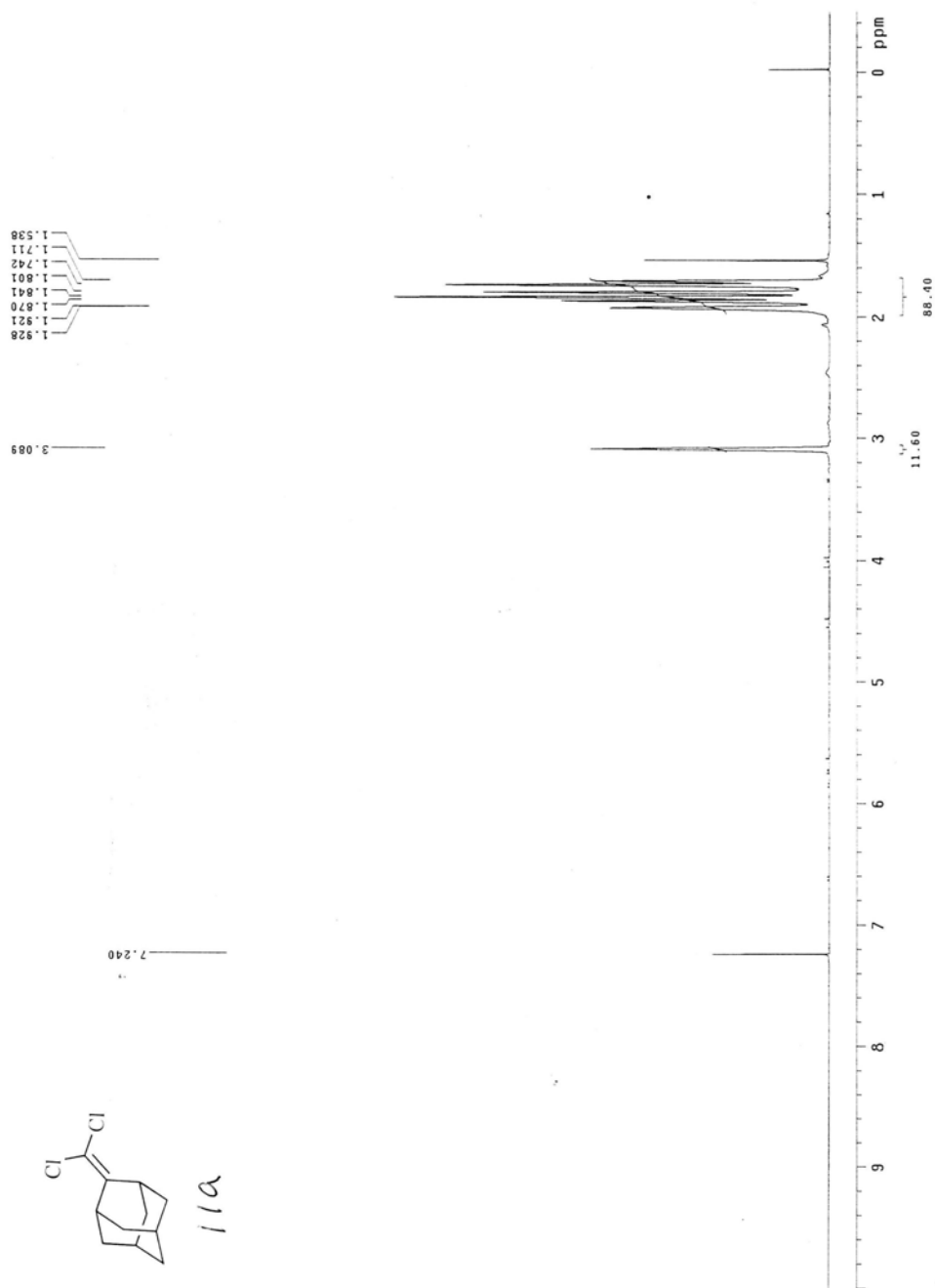


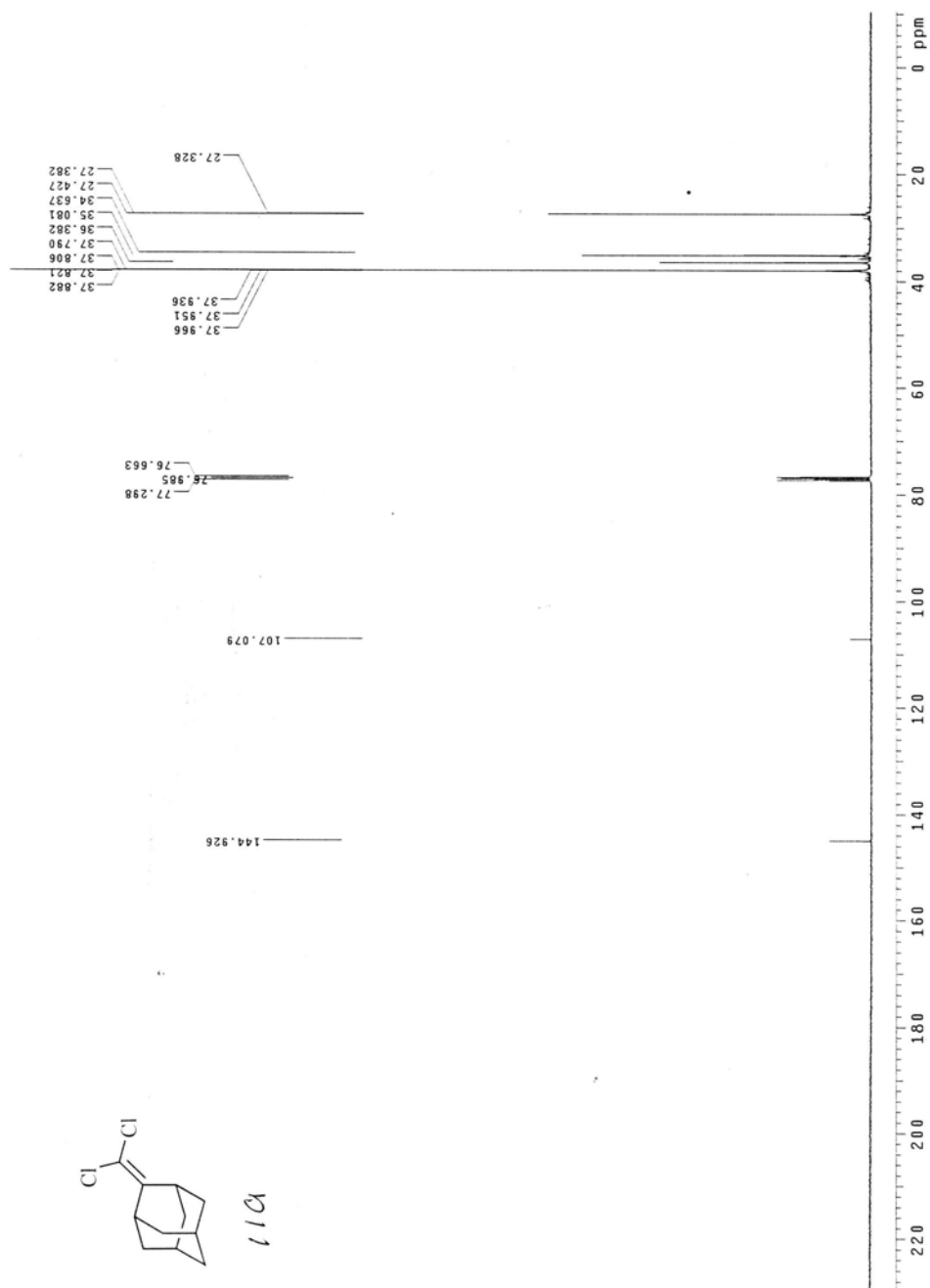
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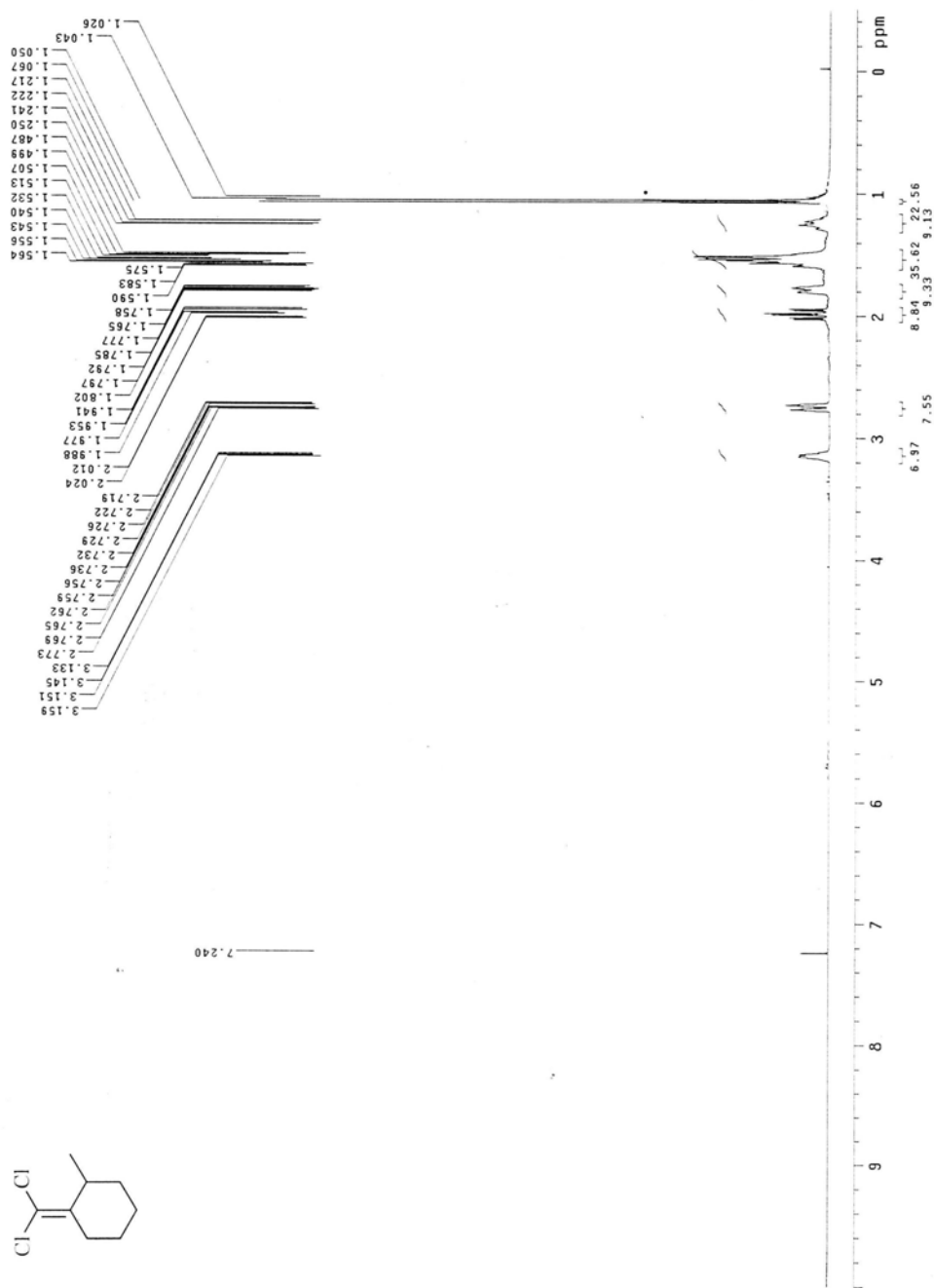
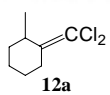


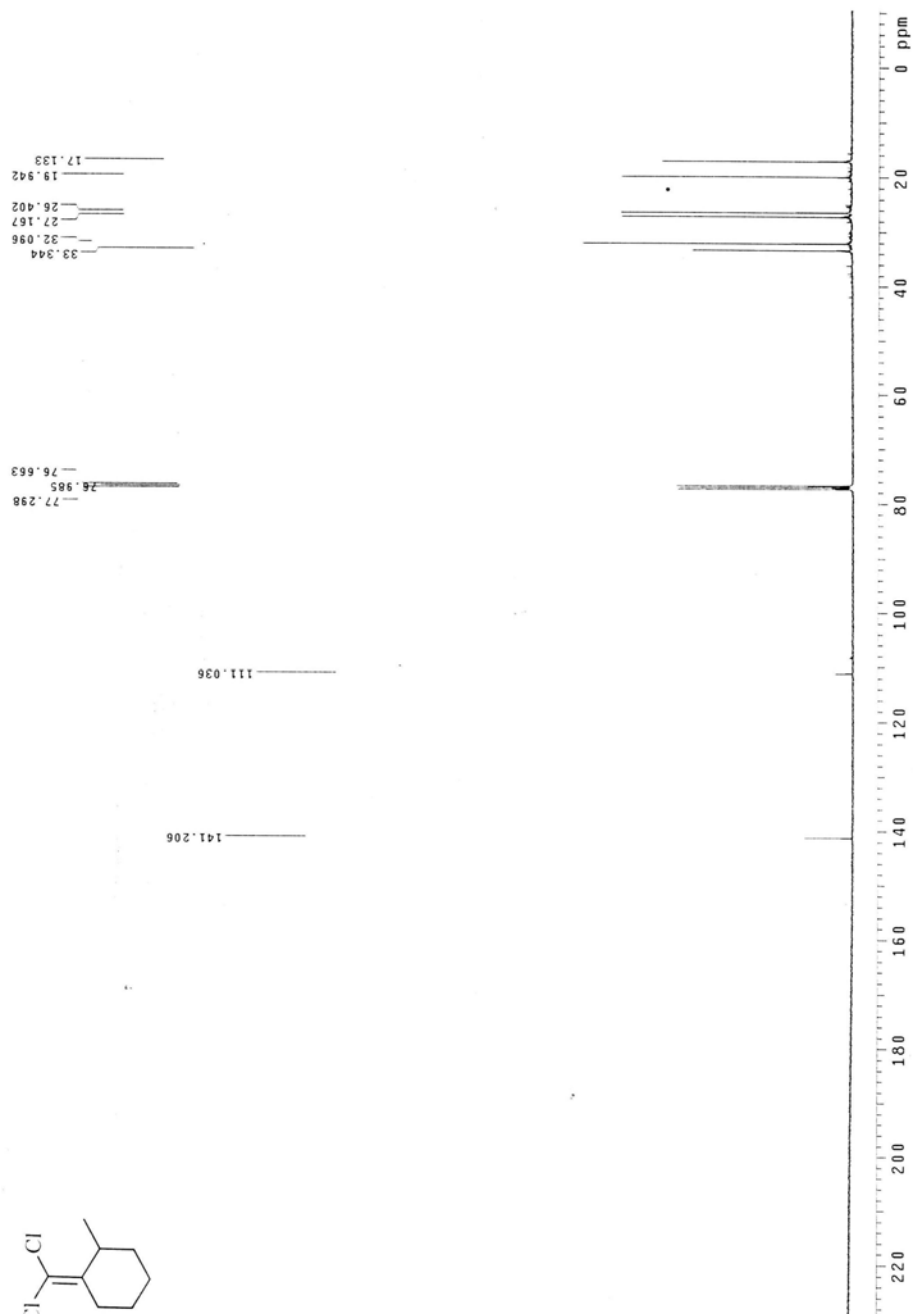
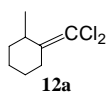


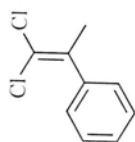
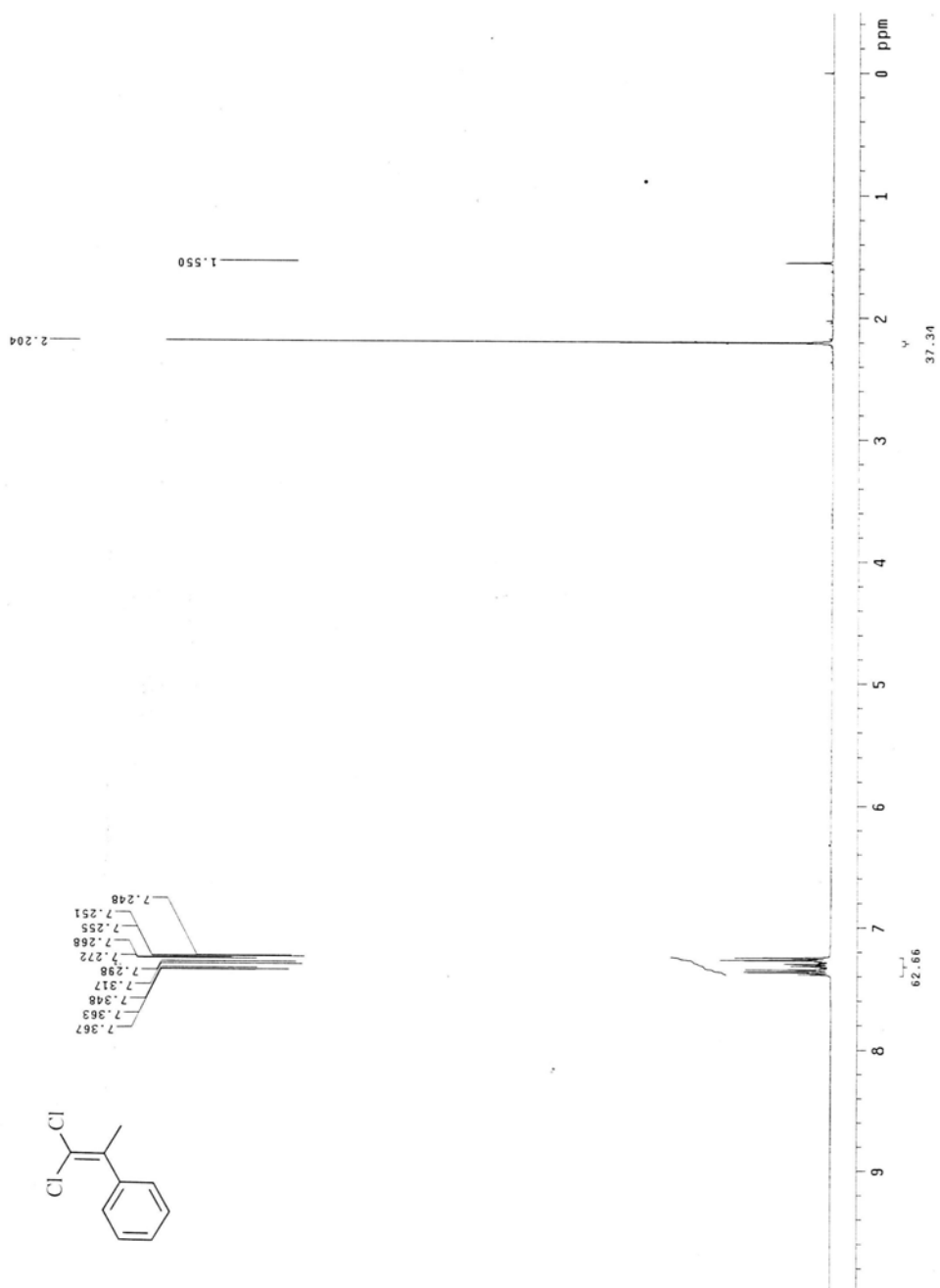
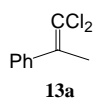


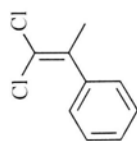
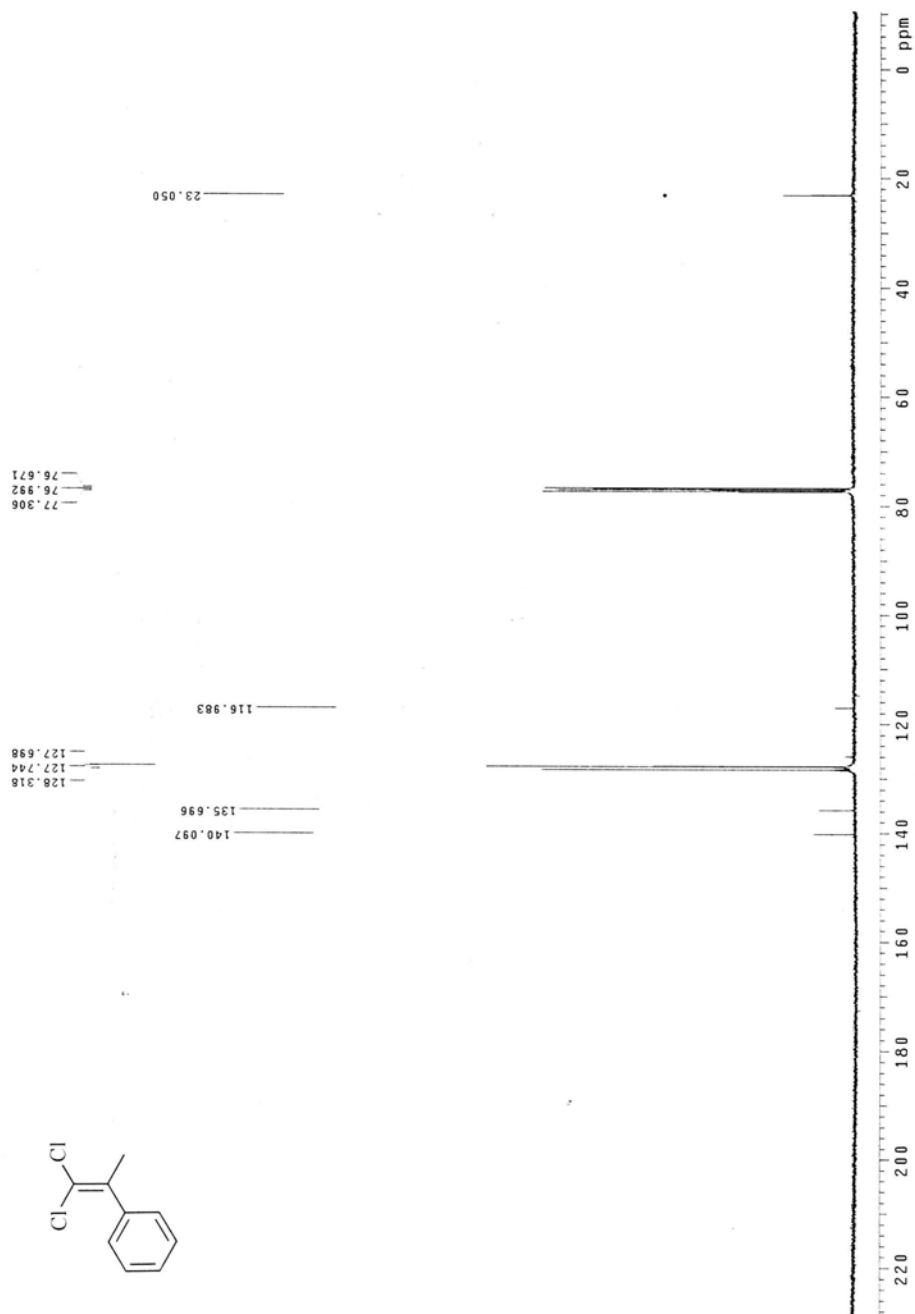
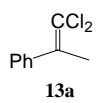


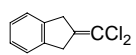




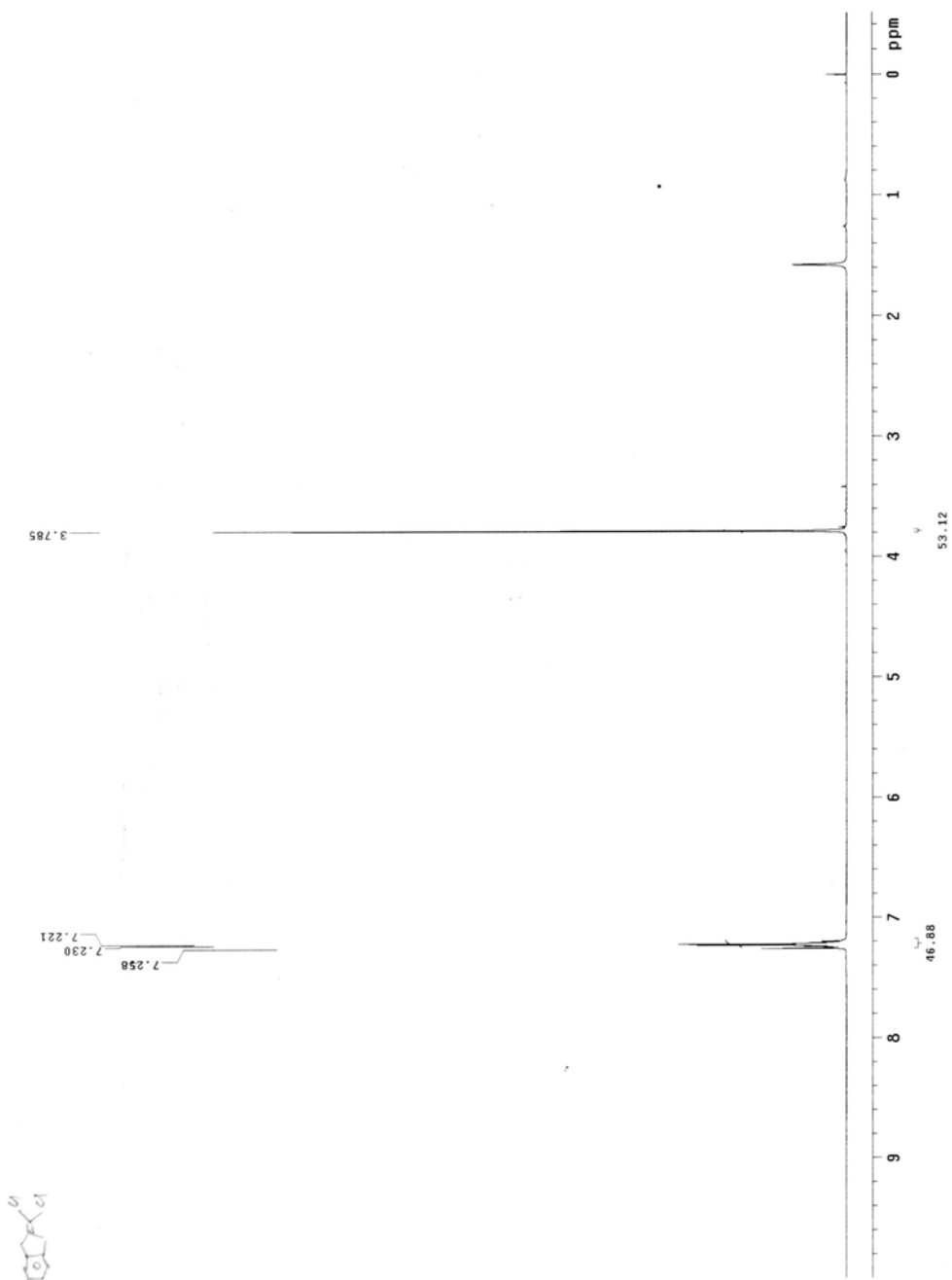


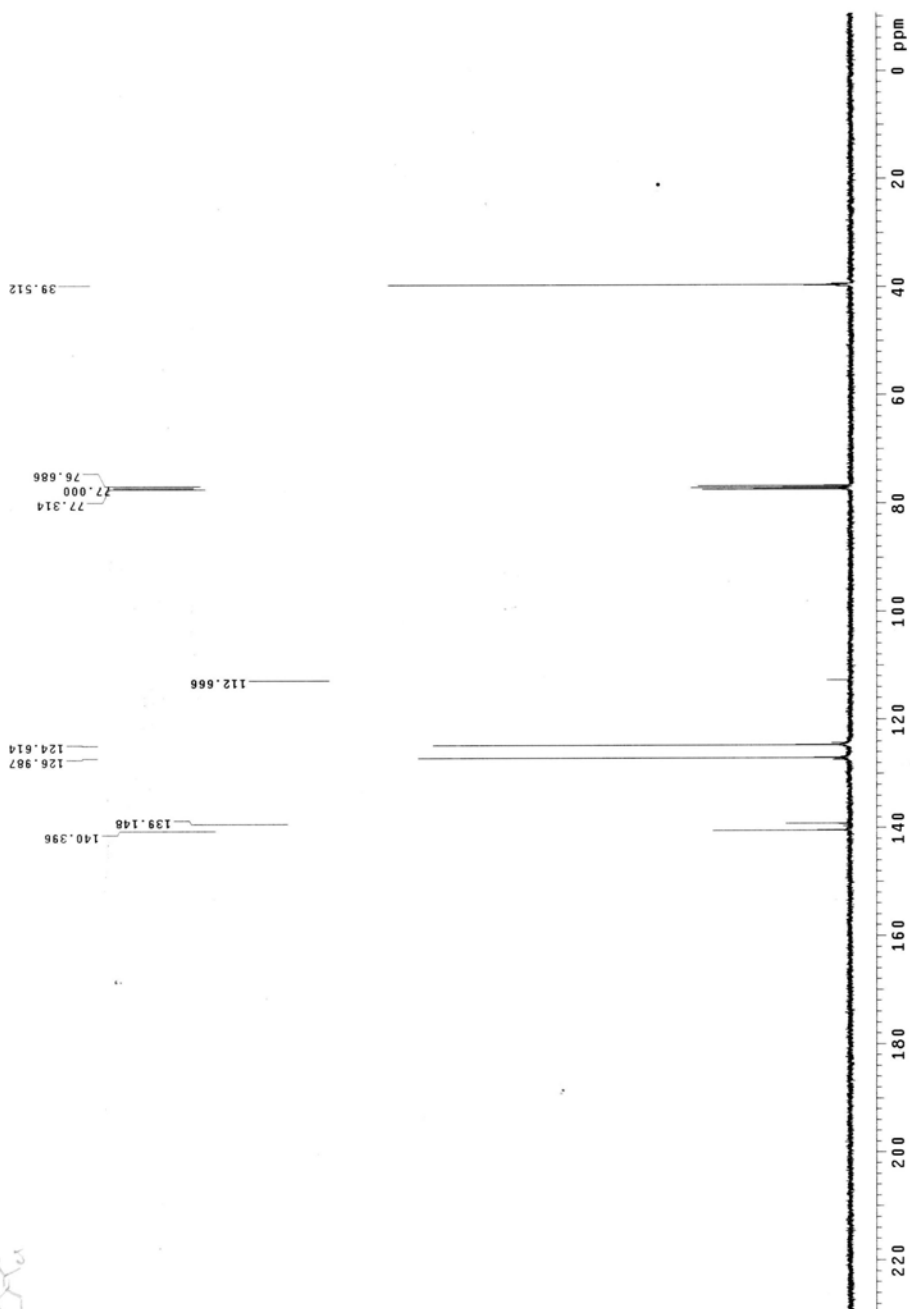






15a





ClC1(Cl)C=C2C=CC=CC=C12
15a

