Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Deca-heterosubstituted corannulenes

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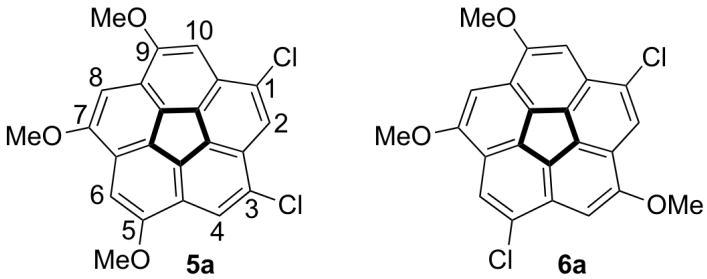
General Methods

All reactions were performed under air, unless stated otherwise. All reagents were purchased from commercial sources and used without further purification. 1,3,5,7,9-pentachlorocorannulene was prepared according to literature procedure.[1] ^{1}H-NMR, ^{13}C-NMR spectra were recorded on a Bruker DPX200 spectrometer, operating at 200MHz (^{1}H), on a Bruker Ultrashield AV300 spectrometer, operating at 300 MHz (^{1}H), 75.44 MHz (^{13}C), on a Bruker AV III 400 spectrometer, operating at 400 MHz (^{1}H), 100.69 MHz (^{13}C) and AV500 operating at 500 MHz (^{1}H), 125.76 MHz (^{13}C). Chemical shifts are reported as δ value in ppm and referenced to Me_4Si (δ=0.0). Mass spectral analysis was performed on a Water Micromass LCT Primier mass spectrometer under electron spray ionization (ESI) or under atmospheric pressure chemical ionization (APCI). CI-MS spectra were measured on a Finnigan TSQ-70 spectrometer and MALDI-TOF spectra were measured on a MALDI Micromass spectrometer using α-cyano-4-hydroxycinnamic acid as a matrix. The reactions under microwave irradiation were performed on a microwave synthesis reactor Monowave 300. TLC was performed on glass sheets pre-coated with silica-gel (Merck, Kieselgel 60, F254, Art.5715). Preparative TLC was performed on glass sheets (Merck, PLC Silica gel 60 F_{254}, 2 mm). Column chromatographic separations were performed on silica-gel (Merck, Kieselgel 60, 230-400 mesh, Art. 9385) under pressure (flash chromatography).

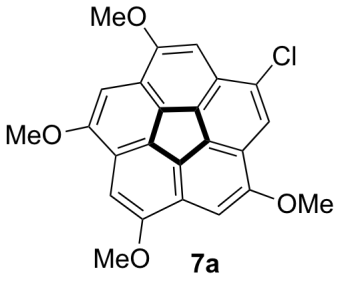
1,3-dichloro-5,7,9-trimethoxycorannulene and 1,5-dichloro-3,7,9-trimethoxyco rannulene (5a and 6a):



(1) S. Mizyed, P. Georghiou, M. Bancu, B. Cuadra, A. K. Rai, P. Cheng, L. T. Scott, *J. Am. Chem. Soc.*, 2001, **123**, 12770.

A stirred solution of **2** (20.9 mg, 0.05 mmol), MeOH (0.3 ml), CuI (5 mg, 0.025 mmol, 0.5 equiv), 1,10-phenanthroline (9 mg, 0.05 mmol, 1 equiv.) and Cs_2CO_3 (0.185 g, 0.57 mmol, 12 equiv.) in DMF (2 ml) was heated to 110 ˚C for 24 hours. Then the mixture was cooled to room temperature, diluted with chloroform (30 ml), washed with 10% HCl aq. (2 × 30 ml), water (2 × 30 ml) and brine (30 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude reaction was purified on preparative TLC plates (EtOAc/Hexanes 1:19) to afford a mixture of two inseparable isomers **5a** and **6a** as yellow solids (6.8 mg, 34%) in a 1:4 ratio, respectively. ^{1}H-NMR (200 MHz, $CDCl_3$) of major isomer **6a**: δ 7.88 (s, 1H), 7.83 (s, 1H), 7.00 (s, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 4.08 (s, 3H), 4.07 (s, 3H), 4.04 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): δ 159.3, 159.0, 158.35, 135.1, 134.7, 131.8, 131.5, 131.5, 131.3, 131.0, 130.8, 130.0, 126.8, 123.95, 123.8, 123.3, 122.1, 100.4, 99.5, 98.8, 56.3, 56.3, 56.25; HRMS (APCI): *m/z* calcd for $C_{23}H_{15}O_3Cl_2$ $[M+H]^+$ 409.0398, found 409.0374.

1-chloro-3,5,7,9-tetramethoxycorannulene (7a):

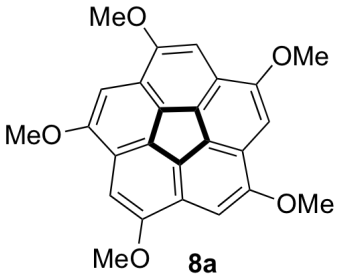


7a

A stirred solution of **2** (20 mg, 0.05 mmol), MeOH (0.3 ml), CuI (5 mg, 0.025 mmol, 0.5 equiv.), 1,10-phenanthroline (9 mg, 0.05 mmol, 1 equiv.) and Cs_2CO_3 (0.185 g, 0.57 mmol, 12 equiv.) in NMP (2 ml) was heated to 145-150 ˚C for 2 days. Then the mixture was cooled to room temperature, diluted with chloroform (30 ml), washed with 10% HCl aq. (2 × 30 ml), water (2 × 30 ml) and brine (30 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was washed with hexanes to afford the desired product **7a** as a yellow-brown solid (12.3 mg, 64%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.04 (s, 1H), 7.00 (s, 2H), 6.97 (s, 1H), 4.08 (s, 3H), 4.05 (s, 6H), 4.04 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): δ 159.4, 158.7, 158.5, 132.2, 131.6, 131.5, 123.0, 125.1, 123.8, 122.0, 99.6,

99.4, 98.7, 56.2; HRMS (APCI): *m/z* calcd for $C_{24}H_{18}O_4Cl$ $[M+H]^+$ 405.0894, found 405.0897.

1,3,5,7,9-pentamethoxycorannulene (8a):



8a

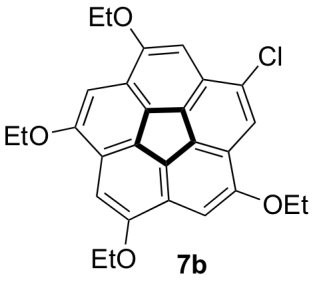
Method A: A solution of **2** (40 mg, 0.095 mmol), MeOH (0.6 ml), CuI (9 mg, 0.05 mmol, 0.5 equiv), 1,10-phenanthroline (17 mg, 0.095 mmol, 1 equiv) and Cs_2CO_3 (0.925 g, 2.85 mmol, 30 equiv) in dry DMSO (2 ml) was heated to 145-150 ˚C for 2 days. After cooling to room temperature the mixture was diluted with chloroform (30 ml) and washed with 10% HCl aq. (2 × 30 ml), water (2 × 30 ml) and brine (30 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford compound **8a** (33.8 mg, 89%) as a yellow-brown solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.03 (s, 5H), 4.05 (s, 15H); ^{13}C (100 MHz, $CDCl_3$): δ 158.6, 132.3, 124.95, 98.5, 56.2; HRMS (ESI): *m/z* calcd for $C_{25}H_{21}O_5$ $[M+H]^+$ 401.1389, found 401.1353.

Method B (Microwave irradiation): Into a 10 ml round-bottomed tube, equipped with a magnetic stirrer, were added **2** (4.7 mg, 0.011 mmol), MeOH (0.1 ml), CuI (1.27 mg, 0.006 mmol, 0.5 equiv.), 1,10-phenanthroline (2.2 mg, 0.011 mmol, 1 equiv.), Cs_2CO_3 (0.110 g, 0.333 mmol, 30 equiv.) and DMSO (0.6 ml). The tube was put into a microwave synthesizer and the reaction was heated to 150 ˚C for 20 min. The workup was identical to the workup described in method A, affording compound **8a** (4.1 mg, 92%) as a yellow-brown solid.

1-chloro-3,5,7,9-tetraethoxycorannulene (7b) and 1,3,5,7,9-pentaethoxycorannulene (8b):

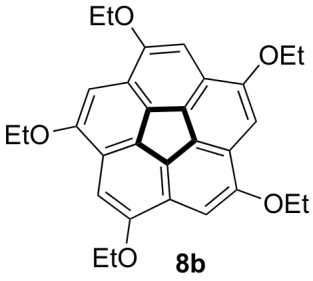
Method A: A stirred solution of **2** (20 mg, 0.05 mmol), EtOH (0.3 ml), CuI (5 mg, 0.025 mmol, 0.5 equiv.), 1,10-phenanthroline (9 mg, 0.05 mmol, 1 equiv.) and Cs_2CO_3 (0.470 g, 1.42 mmol, 30 equiv.) in DMSO (2 ml) was heated to 150-155 ˚C

for 4 days. Then the mixture was cooled to room temperature, diluted with chloroform (30 ml), washed with 10% HCl (2 × 30 ml), water (2 × 30 ml) and brine (30 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude products were separated over preparative TLC plates (EtOAc/Hexanes 1:19) affording first compound **7b** (7 mg, 32%) as a yellow solid, follow by compound **8b** (3.5 mg, 16%) as a yellow solid.



7b

7b: ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.06 (s, 1H), 7.02 (s, 2H), 6.98 (s, 1H), 4.29 (m, 8H), 1.57 (m, 12H); ^{13}C (100 MHz, $CDCl_3$): δ 158.68, 157.99, 157.70, 157.38, 135.17, 132.08, 132.00, 131.64, 131.40, 131.21, 129.84, 126.58, 125.44, 125.19, 125.03, 123.78, 121.91, 100.37, 99.86, 99.35, 64.62, 64.55, 64.51, 64.45, 14.99, 14.94, 14.90, 14.87; HRMS (AP): *m/z* calcd for $C_{28}H_{26}O_4Cl$ $[M+H]^+$ 461.1520, found 461.1517.

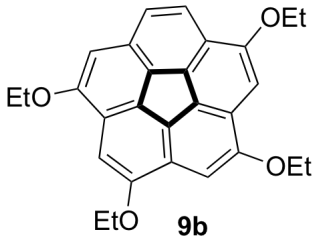


8b

8b: ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.02 (s, 5H), 4.28 (q, J = 6.9 Hz, 10H), 1.56 (t, J=6.9 Hz, 15H); ^{13}C (100 MHz, $CDCl_3$): δ 157.8, 132.3, 125.1, 99.3, 64.5, 15.0; HRMS (APCI): *m/z* calcd for $C_{30}H_{31}O_5$ $[M+H]^+$ 471.2171, found 471.2138.

Method B (Microwave irradiation): Into a 10 ml round-bottomed tube, equipped with a magnetic stirrer, were added **2** (7.4 mg, 0.017 mmol), EtOH (0.1 ml), CuI (1.7 mg, 0.009 mmol, 0.5 equiv), 1,10-phenanthroline (3.16 mg, 0.017 mmol, 1 equiv), Cs_2CO_3 (0.171 g, 0.525 mmol, 30 equiv), and DMF (0.5 ml). The tube was put into a

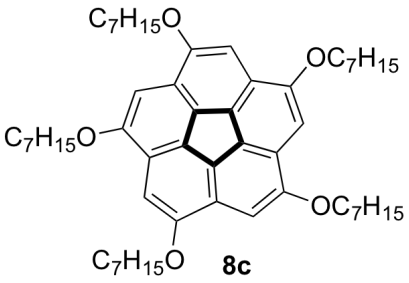
microwave synthesizer and the reaction was heated to 200 ˚C for 2 hours. The workup was identical to the workup described in method A, affording compound **8b** and **9b**. The mixture was separated on preparative TLC plates (100% hexanes) affording compound **8b** (4.7 mg, 57%) as a yellow solid and compound **9b** (3 mg, 40%) as a yellow solid.



9b

9b: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.86 (d, J=8.8 Hz, 1H), 7.62 (d, J=8.8 Hz, 1H), 7.08 (s, 1H), 7.04 (s, 1H), 7. 03 (s, 1H), 6.83 (s, 1H), 4.27 (m, 8H), 1.56 (m, 12H); HRMS (AP): *m/z* calcd for $C_{28}H_{27}O_4$ $[M+H]^+$ 427.1909, found 427.1907.

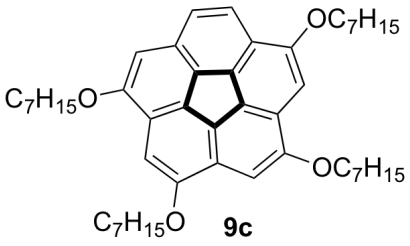
1,3,5,7,9-penta(heptyloxy)corannulene (8c):



8c

Method A: A stirred solution of **2** (84 mg, 0.2 mmol), 1-heptanol (0.85ml, 6 mmol, 30 equiv.), CuI (19 mg, 0.1 mmol, 0.5 equiv.), 1,10-phenanthroline (36 mg, 0.2 mmol, 1 equiv.) and Cs_2CO_3 (1.95 g, 5.9 mmol, 30 equiv.) in DMI (3 ml) was heated to 200 ˚C for 72 hrs. Then the mixture was cooled to room temperature, diluted with dichloromethane (50 mL), washed with 1 N NaOH (3 × 50 mL), 3 M H_2SO_4 (3 × 50 mL), water (50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified over preparative TLC plates (1:9 DCM/Hexane) affording compound **8c** (50 mg, 30%) as a yellow solid and compound **9c** as a yellow solid (31 mg, 22%).

8c: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.01 (s, 5H), 4.20 (m, 10H), 1.95 (m, 10H), 1.54 (m, 10H), 1.42 (m, 10H), 1.30-1.35 (m, 20H), 0.93 (t, 15H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.9, 132.2, 125.3, 99.3, 68.9, 32.0, 29.3, 29.2, 26.3, 22.8, 14.3; MS (ESI) *m/z* calcd for $C_{55}H_{81}O_5$ $[M+H]^+$: 821.6084, found: 821.6054.

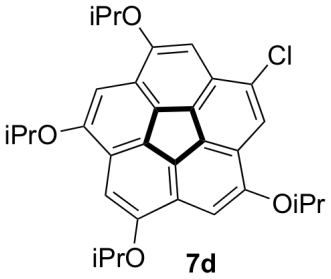


9c

9c: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J*=8.8 Hz, 2H), 7.62 (d, *J*=8.8 Hz, 1H), 7.08 (s, 1H), 7.03 (s, 1H), 7.02 (s, 1H), 6.82 (s, 1H), 4.20 (m, 10H), 1.95 (m, 10H), 1.56 (m, 10H), 1.42 (m, 10H), 1.33 (m, 20H), 0.90 (m, 15H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.4, 158.1, 157.8, 157.7, 136.9, 132.9, 131.95, 131.9, 131.7, 131.4, 126.9, 126.6, 125.4, 125.3, 123.2, 122.8, 103.3, 102.5, 100.4, 99.5, 98.9. 69.0, 68.95, 68.9, 32.0, 32.0, 29.9, 29.3, 29.3, 29.25, 29.2, 26.4, 26.4, 26.35, 22.8, 22.8, 14.3, 14.24; MS (APCI) *m/z* calcd for $C_{48}H_{67}O_4$ $[M+H]^+$: 707.5039, found: 707.5029.

Method B (Microwave irradiation): Into a 10 ml round-bottomed tube, equipped with a magnetic stirrer, were added **2** (5 mg, 0.012 mmol), 1-heptanol (0.2 ml), CuI (1.1 mg, 0.006 mmol, 0.5 equiv), 1,10-phenanthroline (2.2 mg, 0.012 mmol, 1 equiv), Cs_2CO_3 (0.116 g, 0.36 mmol, 30 equiv), and DMF (0.5 ml). The tube was put into a microwave synthesizer and the reaction was heated to 200 ˚C for 1.5 hours and then to 220 ˚C for 1 hour. The workup was identical to the workup described in method A, affording compound **8c** and **9c**. The products were separated on preparative TLC plates (100% hexanes and then 90% hexanes 10% dichloromethane) afford compound **8c** (4 mg, 40%) and side-product **9c** (2 mg, 25%).

1-chloro-3,5,7,9-tetraisopropyloxycorannulene (7d):

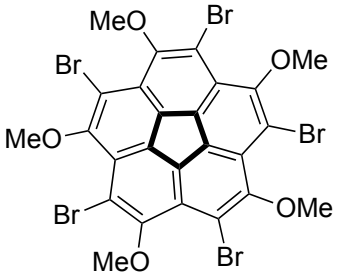


7d

A stirred solution of **2** (20 mg, 0.05 mmol), i-PrOH (0.3 ml), CuI (5 mg, 0.025 mmol, 0.5 equiv.), 1,10-phenanthroline (9 mg, 0.05 mmol, 1 equiv.) and Cs_2CO_3 (0.470 g, 1.42 mmol, 30 equiv.) in dry DMSO (2 ml) was heated to 160-165 ˚C for 5 days. Then the mixture was cooled to room temperature, diluted with chloroform (30 ml), washed with 10% HCl (2 × 30 ml), water (2 × 30 ml) and brine (30 ml). The organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the crude product was purified over preparative TLC plate (EtOAc/hexanes) affording compound **7d** (6 mg, 24%) as a brown solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.08 (s, 1H), 7.042 (s, 1H), 7.037 (s, 1H), 7.02 (s, 1H), 4.86 (m, 4H), 1.47 (m, 24H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.5, 156.8, 156.45, 156.1, 135.5, 132.25, 132.0, 131.8, 131.4, 131.2, 130.0, 129.9, 127.7, 126.5, 126.3, 126.1, 124.8, 122.1, 102.7, 101.6, 71.5, 71.5, 71.4, 71.4, 22.8, 22.2, 22.1, 22.1; HRMS (APCI): *m/z* calcd for $C_{32}H_{34}O_4Cl$ $[M+H]^+$ 517.2146, found 517.2140.

Dechlorination of 2 using *tert*-butanol (Microwave irradiation): Into a 10 ml round-bottomed tube, equipped with a magnetic stirrer, were added **2** (5 mg, 0.012 mmol), *tert*-butanol (0.1 ml), CuI (1.1 mg, 0.006 mmol, 0.5 equiv), 1,10-phenanthroline (2.2 mg, 0.012 mmol, 1 equiv), Cs_2CO_3 (0.116 g, 0.36 mmol, 30 equiv), and DMF (0.5 ml). The tube was put into a microwave synthesizer and the reaction was heated to 220 ˚C for 2 hours. Then the mixture was diluted with dichloromethane (5 mL), washed with 1M HCl (2 × 5 mL), water (5 mL) and brine (5 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The product was purified over a short silica plug (1:4 DCM/Hexane) to afford corannulene (2.1 mg, 71%) as a yellow solid.

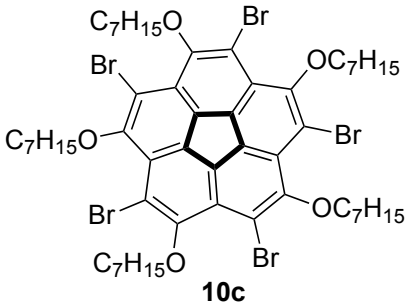
1,3,5,7,9-pentabromo-2,4,6,8,10-pentamethoxycorannulene (10a):



10a

To a stirred solution of **8a** (17.3 mg, 0.043 mmol) in dry DCM (3 ml) at 0 ˚C under argon atmosphere was added dropwise a solution of bromine (0.03 ml, 0.58 mmol, 13.5 equiv.) in DCM (0.5 ml). The reaction was left to stir at room temperature for another 24 hours before it was diluted with dichloromethane (30 ml) and washed with 10% $Na_2S_2O_3$ (3×30 ml), 10% HCl (2×30 ml) and brine (1×30 ml). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford compound **10a** as a brown solid (30 mg, 87%).
^{1}H-NMR (200 MHz, $CDCl_3$): δ 4.16 (s, 15H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.7, 130.0, 126.3, 113.3, 62.9; MS (APCI): *m/z* 778.76 (100%), 780.76 (96%), 782.76 (60%), 776.76 (52%), 774.84 (26%), 784.76 (24%) [M-Me].

1,3,5,7,9-pentabromo-2,4,6,8,10-penta(heptyloxy)corannulene (10c):



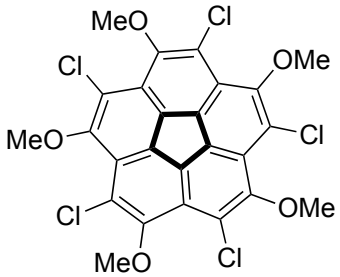
10c

Into a stirred solution of compound **8c** (16 mg, 0.02 mmol) in dry dichloromethane (2.5ml) at -20 ˚C under argon atmosphere was added dropwise bromine (0.02 ml, 0.4 mmol), and the reaction was allowed to warm slowly to room temperature. After 24h chloroform was added and the organic phase was washed with aq. $Na_2S_2O_3$ (2×5 ml), with water (1×5 ml) and brine (1×5 ml). The organic phase was dried over Na_2SO_4,

and the solvent was removed under reduced pressure. Hexane was added to the brown residue to wash it, and the filtrate was concentrated and triturated with ethanol, to give **10c** as an orange solid (10 mg, 42%).

^{1}H-NMR (300 MHz, CD_2Cl_2): δ 4.22 (m, 10H), 2.08 (m, 10H), 1.62 (m, 10H), 1.46 (m, 10H), 1.37 (m, 20H), 0.93 (t, 15H); ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 155.0, 130.2, 126.8, 113.8, 76.6, 32.5, 30.3, 29.9, 26.5, 23.3, 14.5; MS (APCI) *m/z* calcd for $C_{55}H_{676}O_5Br_5$ $[M+H]^+$: 1211.1610, found: 1211.1624.

1,3,5,7,9-pentachloro-2,4,6,8,10-pentamethoxycorannulene (11a):

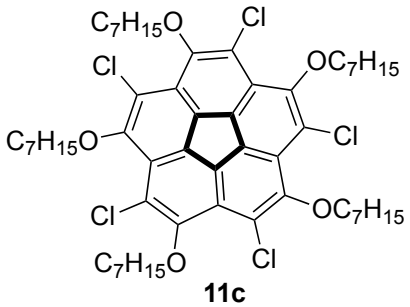


11a

To a stirred solution of **8a** (20.6 mg, 0.051 mmol) in thionyl chloride (3 ml) was added dry DMF (a few drops) and the reaction was heated to 80 ˚C for 8 hrs. Then the mixture was cooled to room temperature, diluted with dichloromethane (20 ml), and slowly poured into a 10% $NaHCO_3$ solution. The organic layer was separated, washed with 10% $NaHCO_3$ solution (2 × 50 ml), water (2 × 50 ml), brine (50 ml), dried over $MgSO_4$ and the solvent was removed under reduced pressure affording product **11a** (23 mg, 78%) as a yellow solid.

^{1}H-NMR (200 MHz, $CDCl_3$): δ 4.16 (s, 15H); ^{13}C (125 MHz, $CDCl_3$): δ 154.5, 128.9, 125.1, 114.1, 62.75; MS (APCI): *m/z* 557.01 (100%), 555.01 (66%), 559.01 (60%), 561.09 (24%) [M-Me].

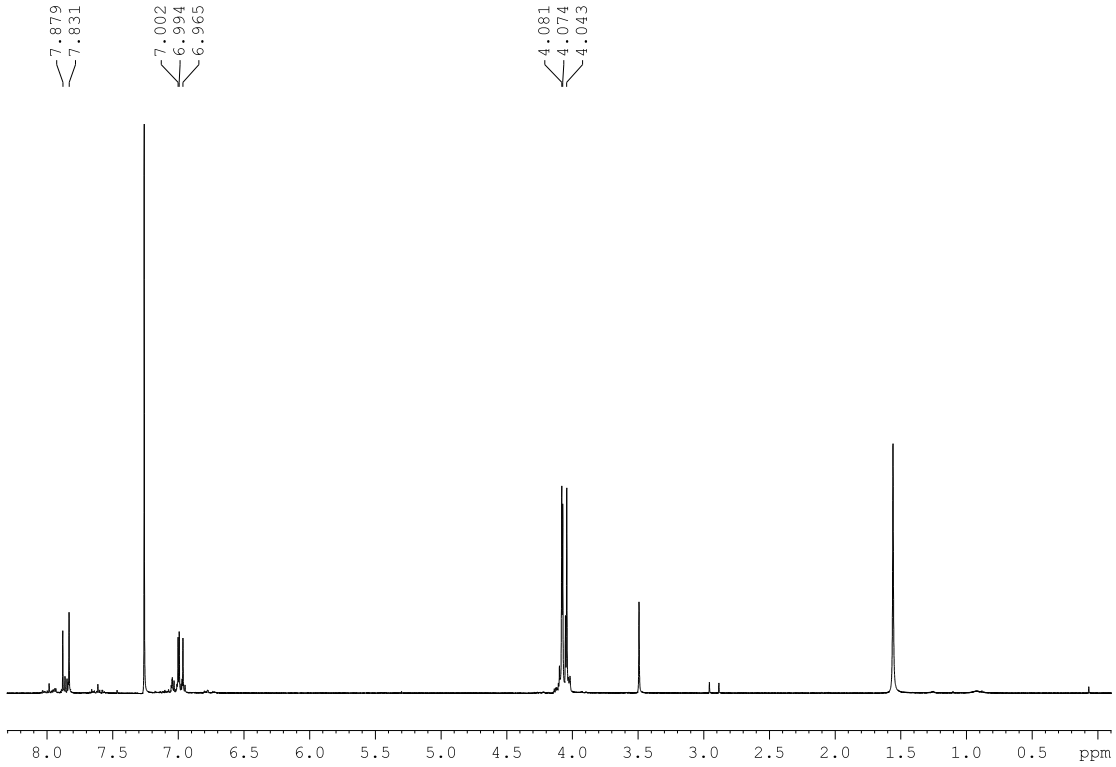
1,3,5,7,9-pentachloro-2,4,6,8,10-pentaheptyloxycorannulene (11c):



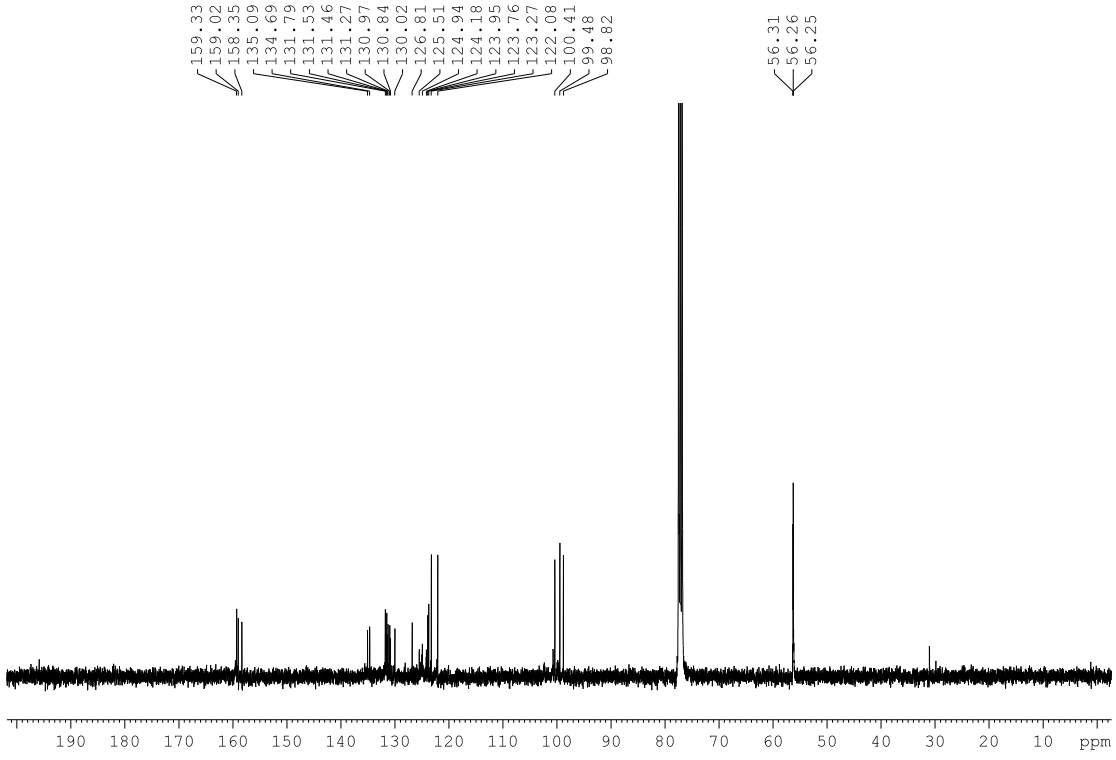
11c

To a stirred solution of **8c** (44 mg, 0.03 mmol) in thionyl chloride (2 ml) under argon atmosphere was added dry DMF (a few drops) and the reaction was heated to 80 ˚C for 18 hrs. Then the mixture was cooled to room temperature, the solvent was distilled off and dichloromethane (10 ml) was added. The organic phase was washed with a concentrated $NaHCO_3$ solution (3 × 10 ml), brine (10 ml), dried over Na_2SO_4 and the solvent was removed under reduced pressure to afford product **11c** (33 mg, 62%). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 4.23 (m, 10H), 2.03 (m, 10H), 1.76 (m, 10H), 1.61 (m, 10H), 1.45-47 (m, 20H), 0.92 (t, 15H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.9, 129.0, 125.5, 124.1, 76.4, 32.2, 30.4, 29.6, 26.3, 23.0, 14.2; MS (MALDI TOF LD-) *m/z*: 891.8 (M-Hept-H, 100%), 792.8 (M-2Hept-2H, 77%), 694.0 (M-3Hept-H, 51%), 595.4 (M-4Hept, 28%), 497.0 (M-5Hept, 46%).

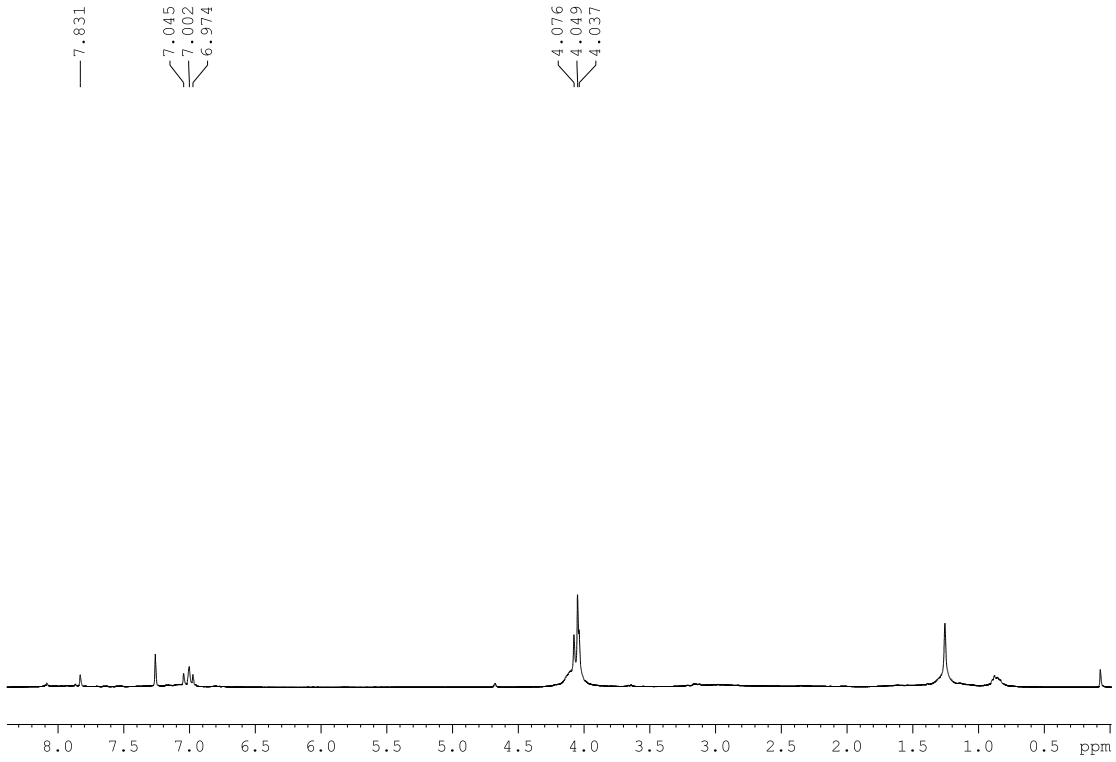
^{1}H NMR of isomers **5a** and **6a** (300 MHz, $CDCl_3$):



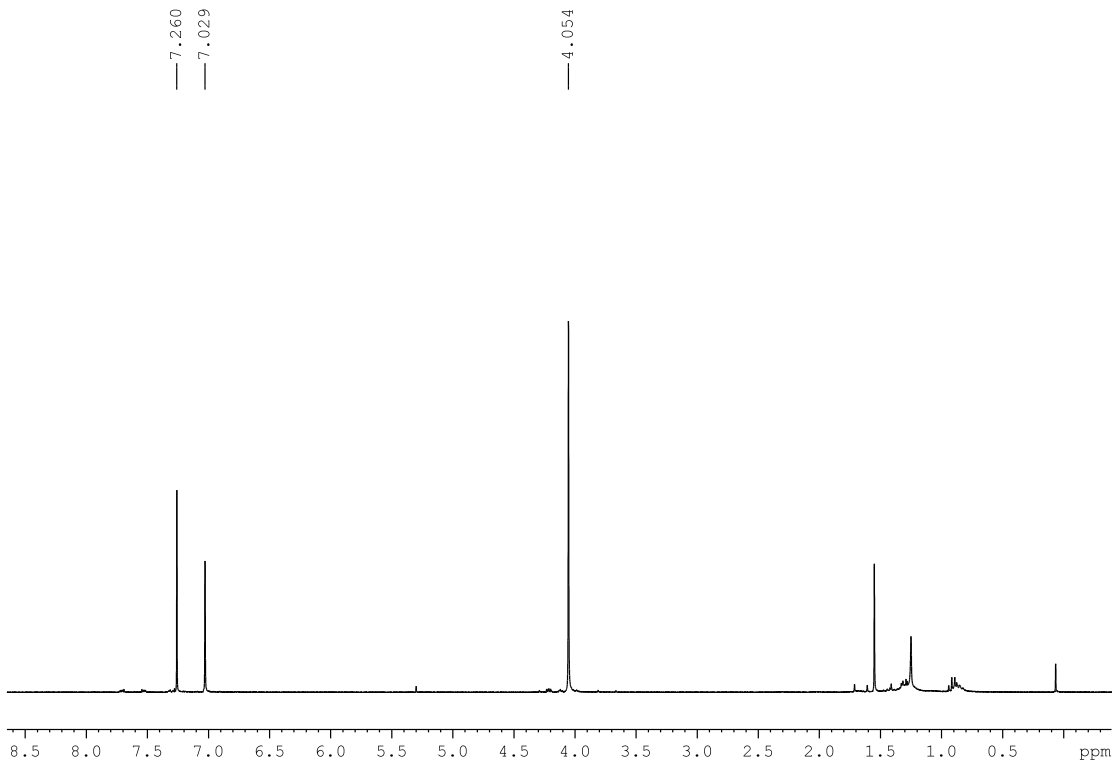
^{13}C NMR of isomers **5a** and **6a** (100 MHz, $CDCl_3$):



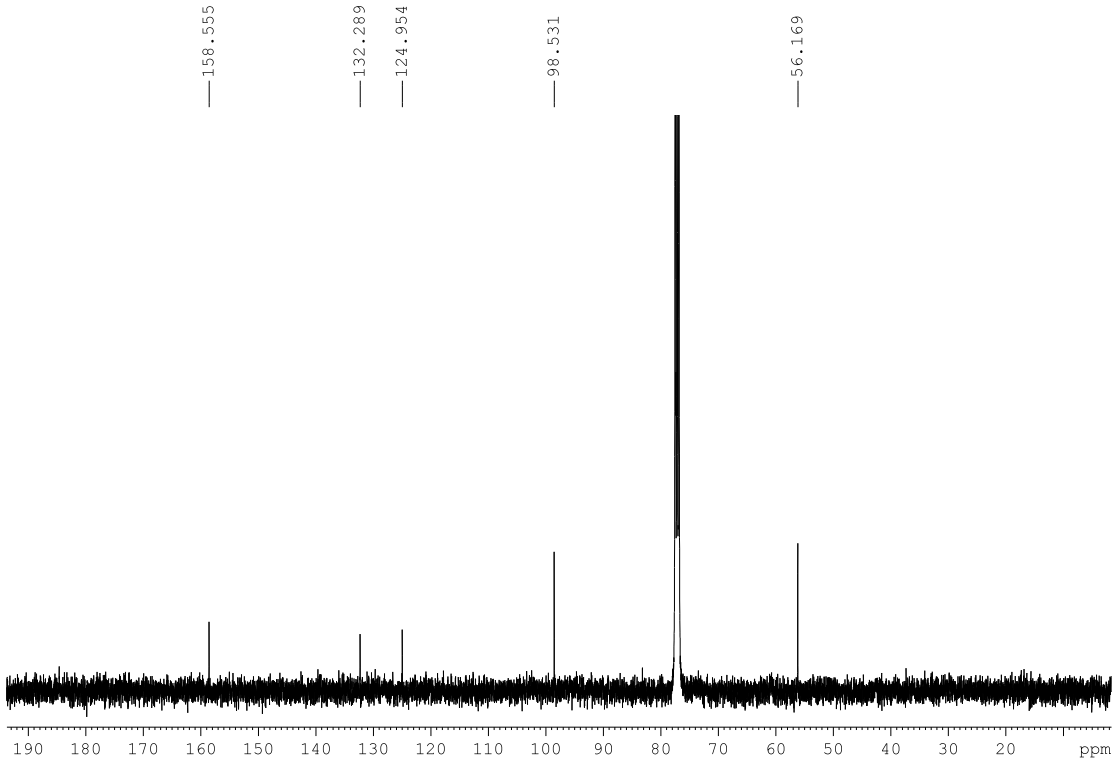
^{1}H NMR of compound **7a** (400 MHz, $CDCl_3$):



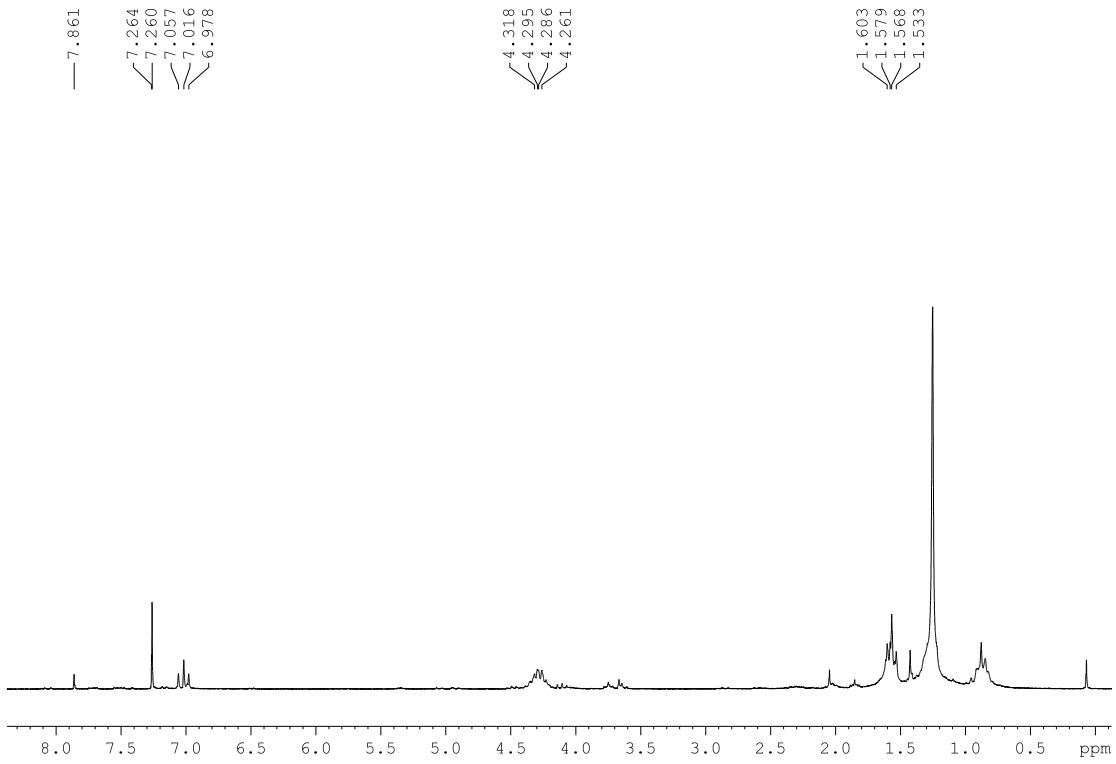
^{1}H NMR of compound **8a** (300 MHz, $CDCl_3$):



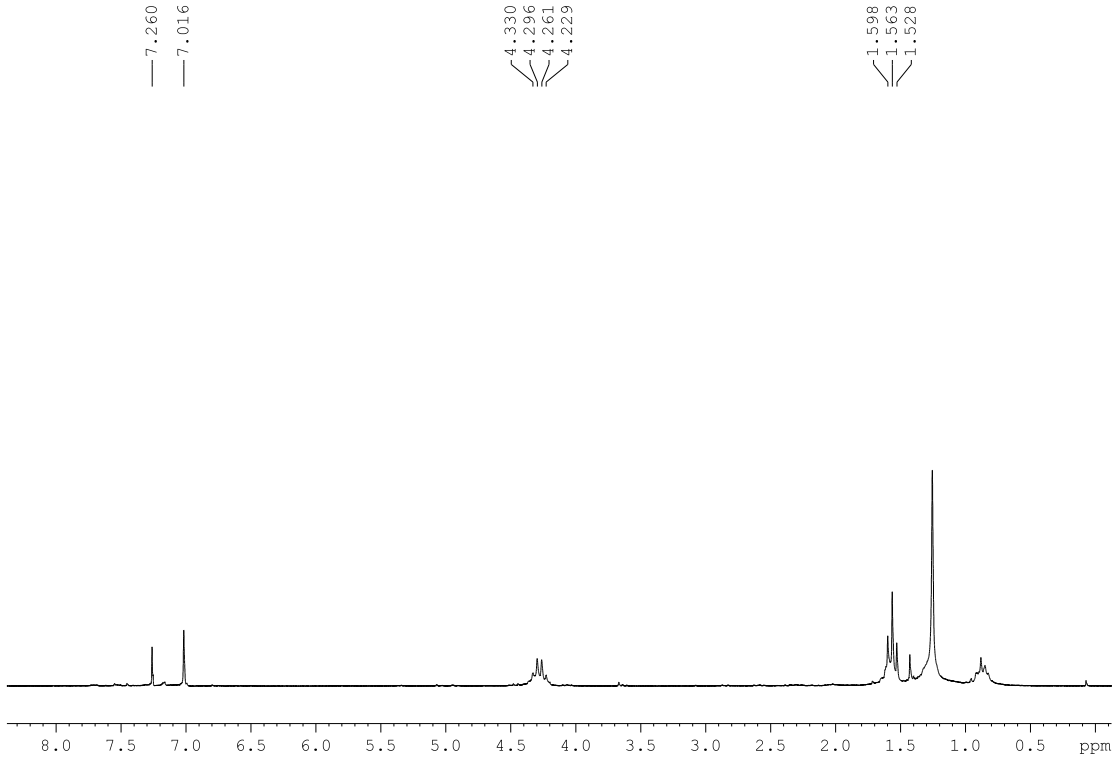
^{13}C NMR of compound **8a** (100 MHz, $CDCl_3$):



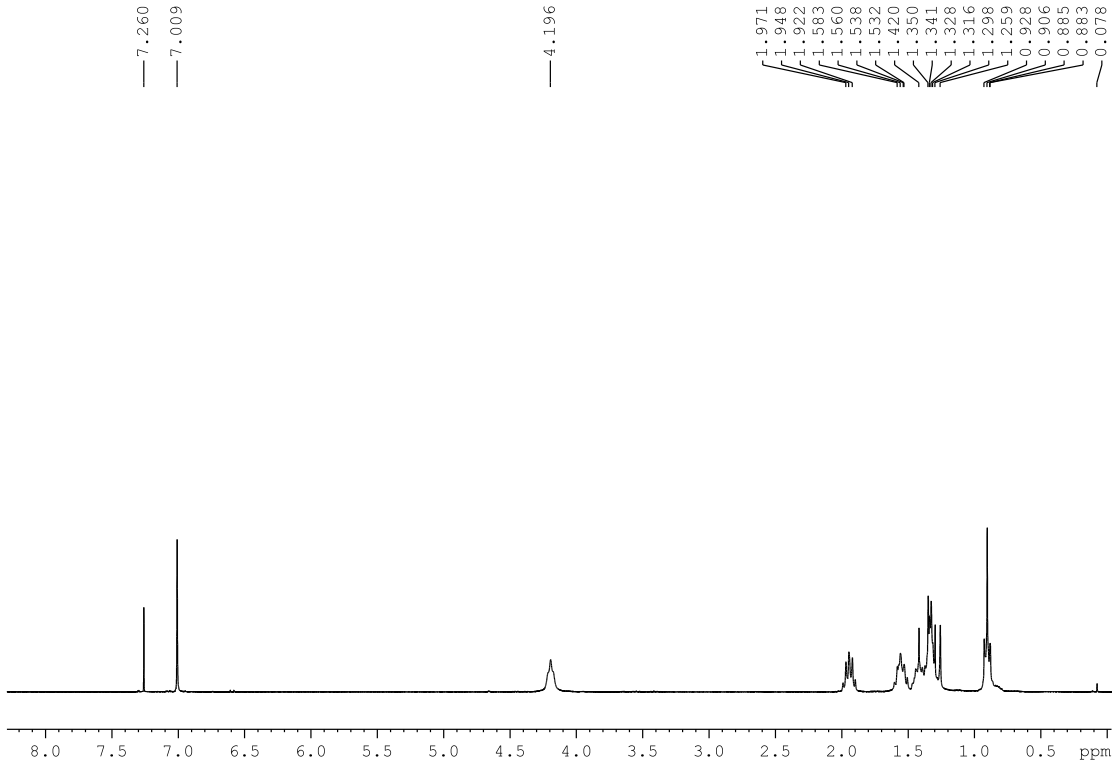
^{1}H NMR of compound **7b** (200 MHz, $CDCl_3$):



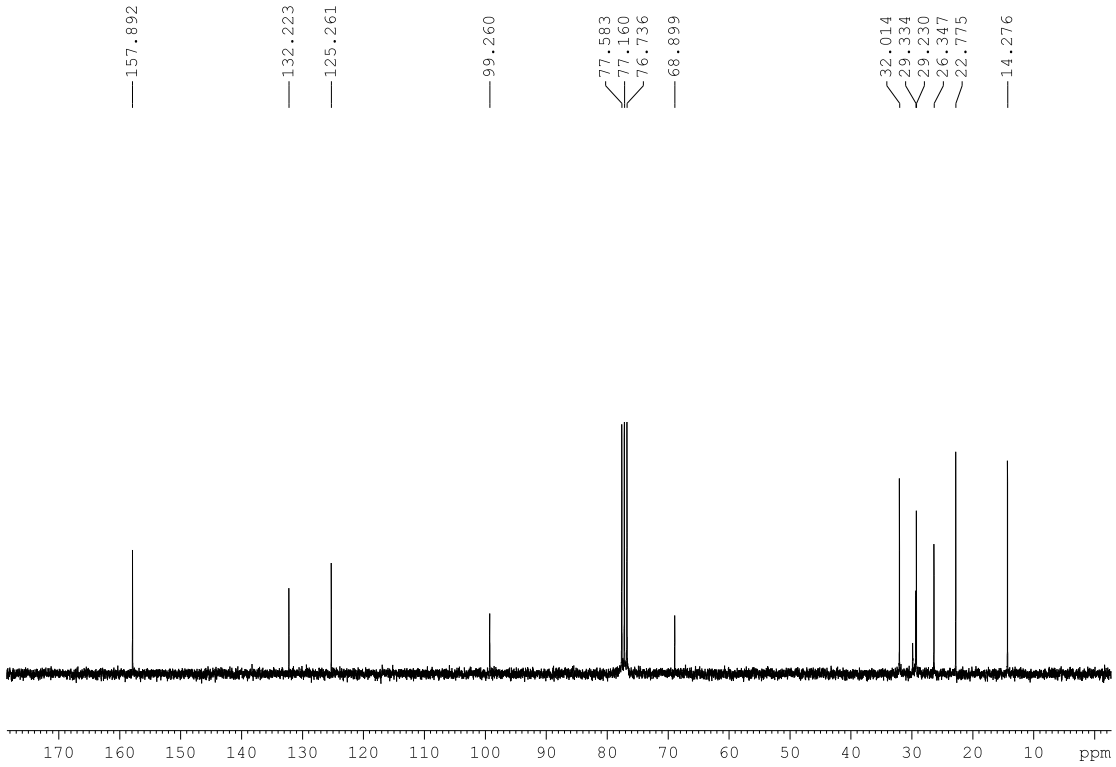
^{1}H NMR of compound **8b** (200 MHz, $CDCl_3$):



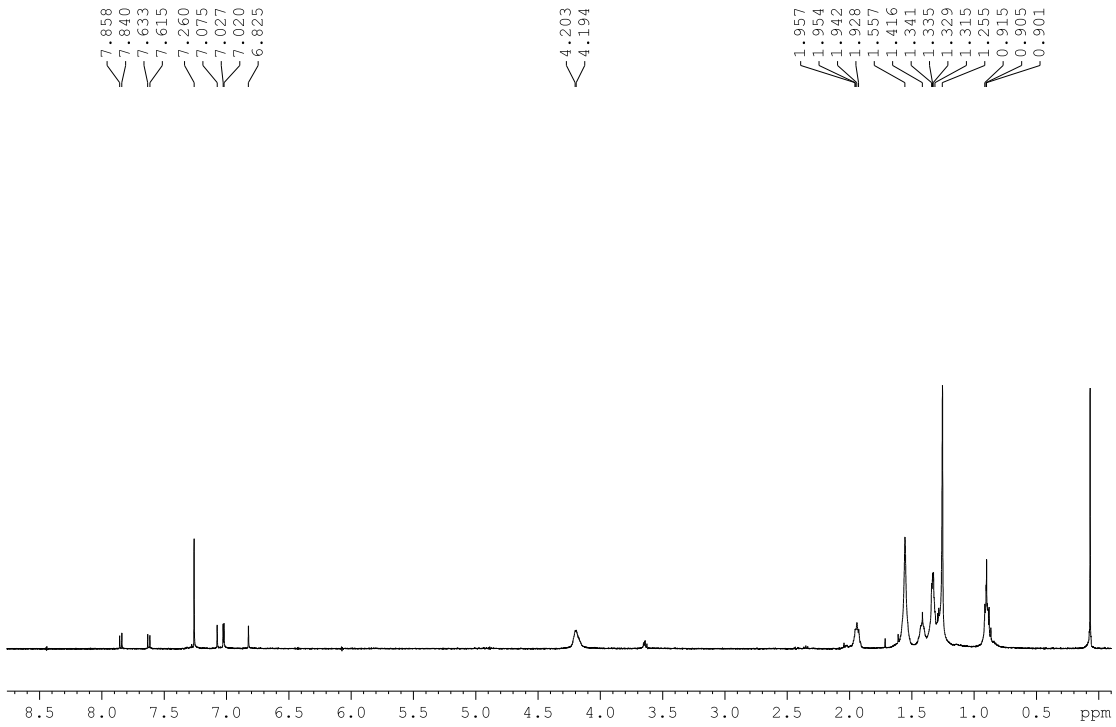
^{1}H NMR of compound **8c** (300 MHz, $CDCl_3$):



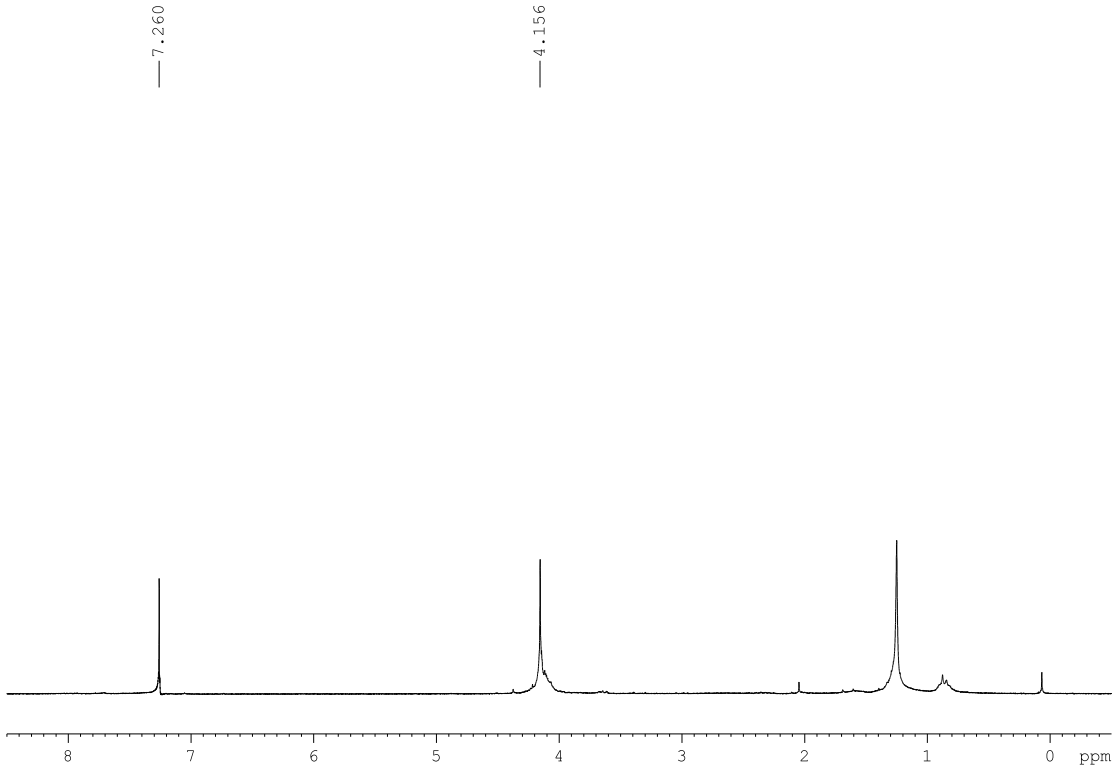
^{13}C NMR of compound **8c** (75 MHz, $CDCl_3$):



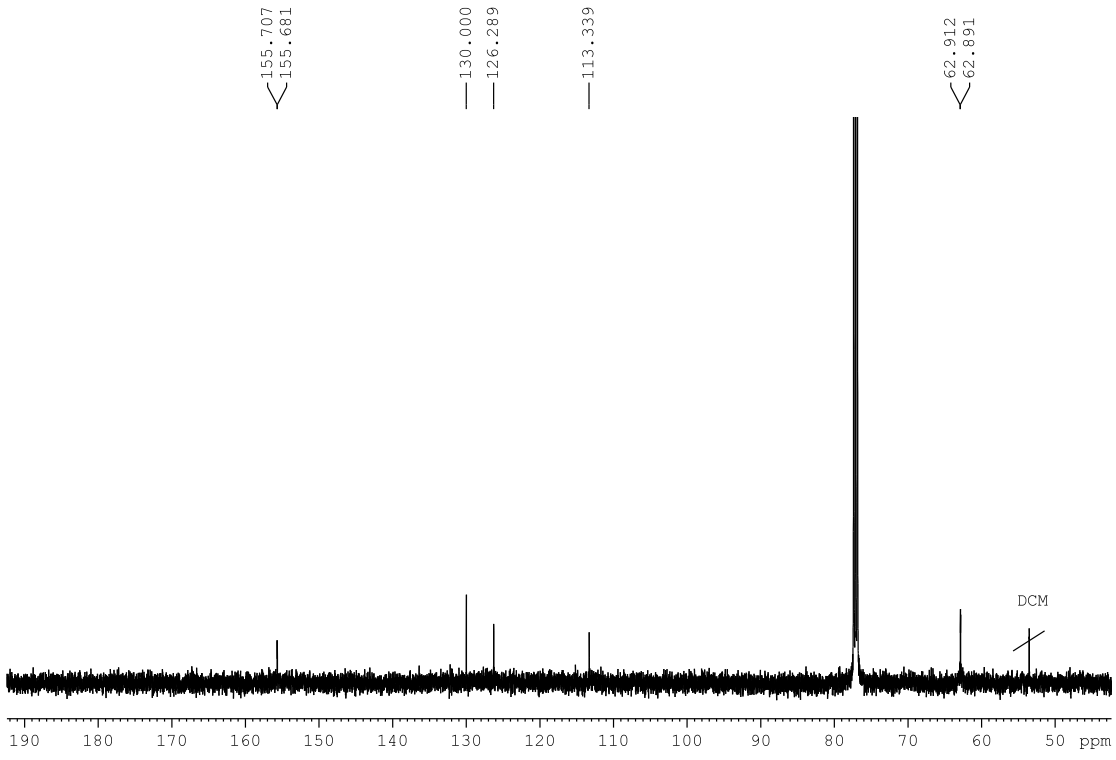
^{1}H NMR of compound **9c** (500 MHz, $CDCl_3$):



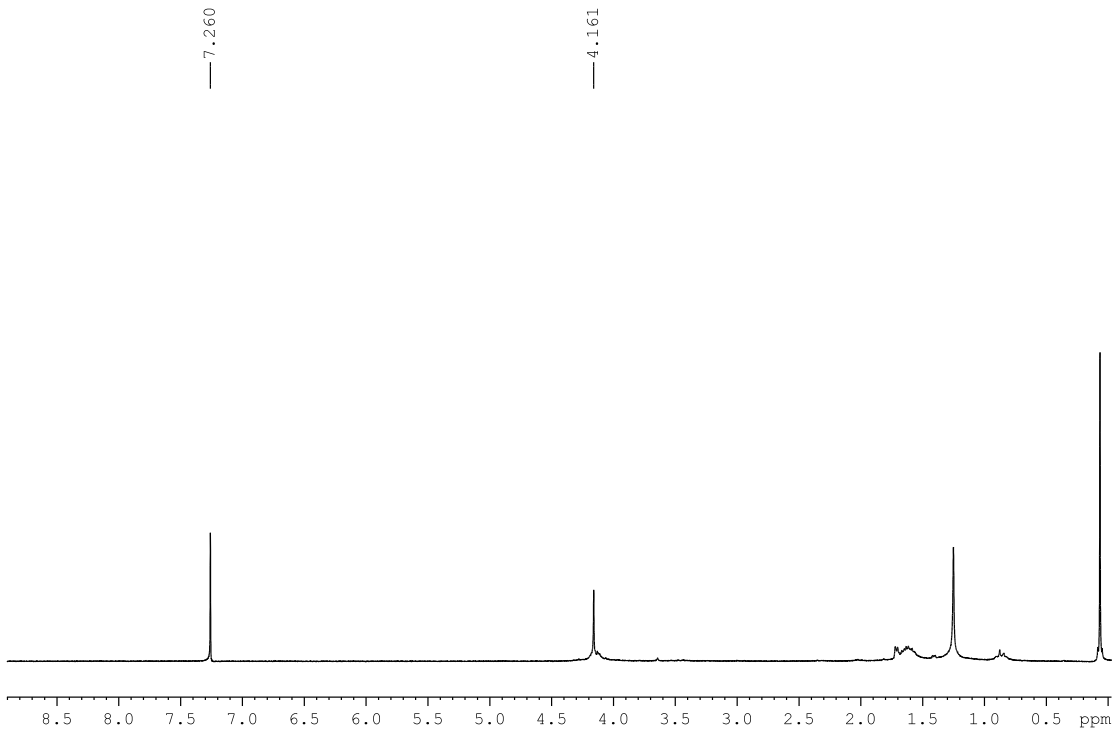
^{1}H NMR of compound **10a** (200 MHz, $CDCl_3$):



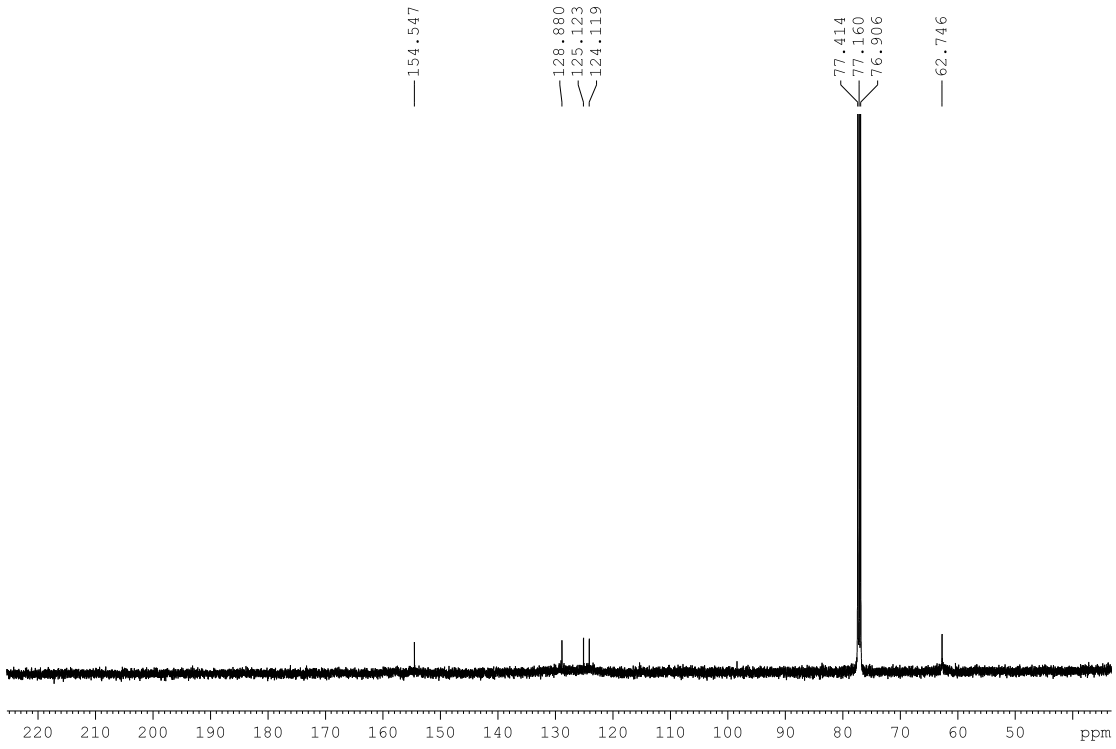
^{13}C NMR of compound **10a** (125 MHz, $CDCl_3$):



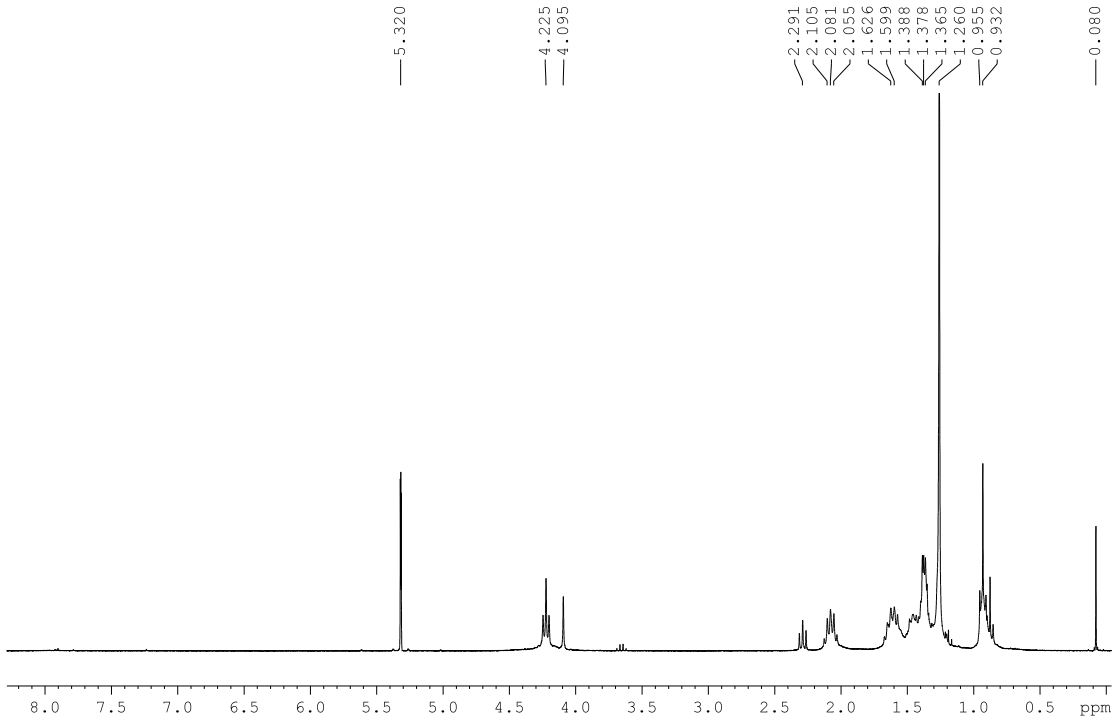
^{1}H NMR of compound **11a** (200 MHz, $CDCl_3$):



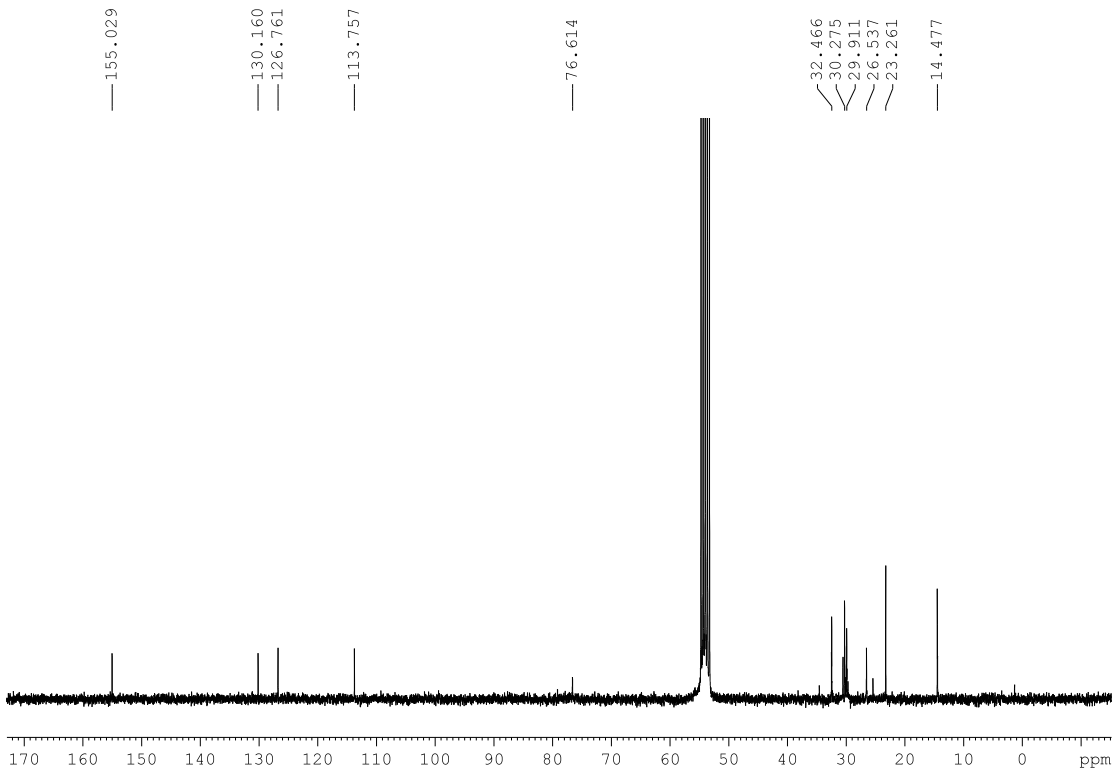
^{13}C NMR of compound **11a** (125 MHz, $CDCl_3$):



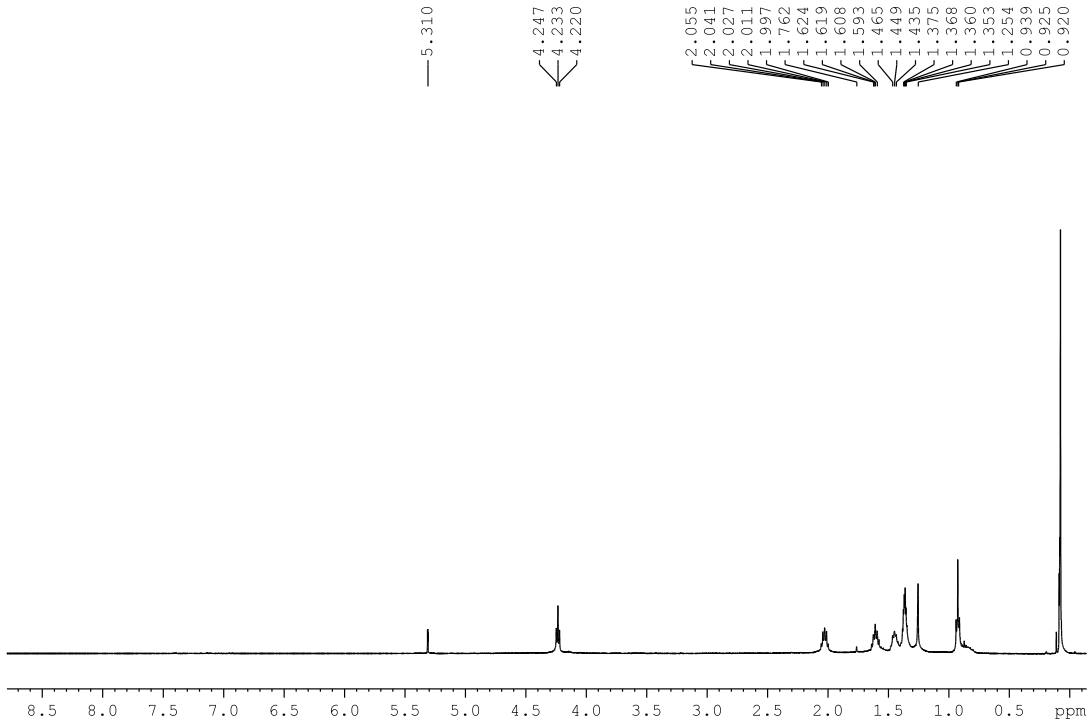
^{1}H NMR of compound **10c** (300 MHz, CD_2Cl_2):



^{13}C NMR of compound **10c** (75 MHz, CD_2Cl_2):



^{1}H NMR of compound **11c** (500 MHz, CD_2Cl_2):



^{13} C NMR of compound **11c** (125 MHz, CD_2Cl_2):