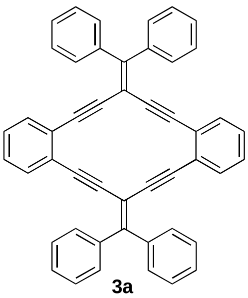
Supplementary Material (ESI) for Chemical Communications

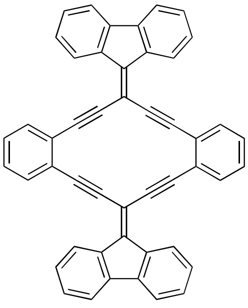
Supporting Information for:

Radiaannulenes: Synthesis, electrochemistry, and solid-state structure

*Mojtaba Gholami, Manuel N. Chaur, Myron Wilde, Michael J. Ferguson, Robert McDonald, Luis Echegoyen, and Rik R. Tykwinski**


3a

Compound 3a. A mixture of compound **5**[1] (107 mg, 0.288 mmol) and K_2CO_3 (8 mg, 0.06 mmol) in THF (1 mL) and MeOH (1 mL) was stirred for 1 h. Et_2O and H_2O were added, the organic phase separated, washed with saturated NH_4Cl (2 x 20 mL), dried ($MgSO_4$), and reduced to 2 mL. This ethereal solution of **6** was deoxygenated* and added to a deoxygenated mixture of 1,2-diiodobenzene (95 mg, 0.288 mmol), CuI (15 mg, 0.08 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), *i*Pr_2NH (3 mL) in dry THF (5 mL). The resulting mixture was refluxed under a N_2 atmosphere for 18 h. After the reaction was cooled, solvent removal and purification by column chromatography (silica gel, hexanes/CH_2Cl_2 7:1 to 3:1) and then re-crystallization from CH_2Cl_2 by the addition of hexanes gave **3a** (27 mg, 31%) as a pale yellow solid. Mp >300 °C (decomp.); R_f = 0.43 (hexanes/CH_2Cl_2 1:1); UV-vis (THF) λ_{max} 413 nm; IR (CH_2Cl_2, cast) 3078, 3050, 3022, 2924, 2852, 2194 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.59–7.57 (m, 8H), 7.45–7.43 (m, 12H), 7.23–7.21 (m, 4H), 7.08–7.06 (m, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 157.6, 140.7, 132.2, 131.1, 129.3, 128.5, 128.1, 125.4, 102.2, 92.9, 90.7. EI HRMS calcd. for $C_{48}H_{28}$ (M^+) 604.2186, found 604.2185. MALDI TOF HRMS calcd. for $C_{48}H_{28}$ (M^+) 604.2186, found 604.2185.


3b

Compound 3b. Compound **11** (64 mg, 0. 15 mmol) was dissolved in ether (8 mL) and the solution deoxygenated.* The deoxygenated ethereal solution of **11** was added to a deoxygenated mixture of **9**[2] (50 mg, 0.15 mmol), CuI (9 mg, 0.05 mmol), $Pd(PPh_3)_4$ (9 mg, 0.008 mmol), *i*Pr_2NH (3 mL) in dry THF (5 mL). The resulting mixture was refluxed under a N_2 atmosphere for 20 h. The reaction crude was cooled washed with saturated NH_4Cl (2 X 20 mL), H_2O (40 mL) and extracted with CH_2Cl_2. After removing the solvent, a solution of hexanes/CH_2Cl_2 (50 mL, 1:1) was added resulting in dispersed red solid. The solid was filtered on a fritted funnel (a 10–20 microns), the solid washed with hexanes (~500 mL) on the frit, and then allowed to air dry. This **3b** (81 mg, 90%) as a highly insoluble red solid. Mp >300 °C (decomp.); R_f = 0.4 (hexanes/CH_2Cl_2 1:1); UV-vis (THF) λ_{max} 345, 446, 472 nm; IR (CH_2Cl_2, cast) 3055, 2960, 2925, 2856 cm^{-1}; ^1H NMR

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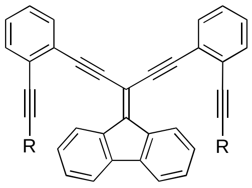
* Solutions were deoxygenated by bubbling N_2 through the solution for ca. 30 min.

(500 MHz, $C_2D_2Cl_4$) δ 8.85–8.33 (m, 4H), 7.80–7.79 (m, 4H), 7.75–7.74 (m, 4H), 7.56–7.54 (m, 4H), 7.47–7.45 (m, 8H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 65 °C) δ 146.1, 140.3, 137.4, 131.8, 129.8, 128.9, 127.4, 125.54, 125.47, 119.7, 101.1, 96.0, 93.1. MALDI TOF HRMS calcd. for $C_{48}H_{24}$ (M^+) 600.1873, found 600.1870.



9 R = S*i*-Pr$_3$i **10** R = H

Compound 11. A mixture of compound **7**[3] (150 mg, 0.423 mmol) and K_2CO_3 (13 mg, 0.09 mmol) in a mixture of THF (2 mL) and MeOH (2 mL) was stirred for 1 h. Et_2O and H_2O were added, the organic phase separated, washed with saturated NH_4Cl (2 x 20 mL), dried ($MgSO_4$), and reduced to 2 mL. This ethereal solution of **8** was deoxygenated* and added to a deoxygenated* mixture of **9** (71 mg, 0.21 mmol), CuI (12 mg, 0.06 mmol), $Pd(PPh_3)_4$ (24 mg, 0.02 mmol), *i*Pr_2NH (3 mL) in dry THF (5 mL). The resulting mixture was refluxed under a N_2 atmosphere for 20 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH_2Cl_2 5:1) afforded **10**[†] as an orange liquid. To a solution of **10** in THF (2 mL) was added TBAF (0.2 mL, 0.2 mmol, 1M in THF) and the mixture stirred at rt for 30 min. Et_2O and H_2O were added, the organic phase separated, washed with saturated NH_4Cl (2 x 20 mL), and dried ($MgSO_4$). Solvent removal and column chromatography (silica gel, hexanes/ CH_2Cl_2 4:1) gave **11** (68 mg, 75%) as a yellow solid. Mp >300 °C (decomp.); R_f = 0.6 (hexanes/CH_2Cl_2 1:1); UV-vis (THF) λ_{max} (ε) nm 396 (26700), 414 (26200); IR (CH_2Cl_2, cast) 3289, 3059, 2926, 2181, 2108 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.33 (d, J = 7.6 Hz, 2H), 7.03–7.00 (m, 4H), 6.96–6.94 (m, 2H), 6.79–6.70 (m, 6H), 6.64 (td, J = 7.6, 1.2 Hz, 2H), 2.78 (s, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 145.8, 140.7, 137.6, 133.4, 132.9, 130.3, 129.34, 129.25, 127.8, 126.4, 126.0, 124.8, 120.0, 100.9, 97.1, 92.6, 82.5, 82.1. MALDI TOF HRMS calcd. for $C_{34}H_{18}$ (M^+) 426.1403, found 426.1403.

[†] For unknown reasons, compound **10** appears to be unstable to chromatographic separation on either silica gel or alumina oxide supports. It was thus taken on directly to the desilylation step without additional purification.

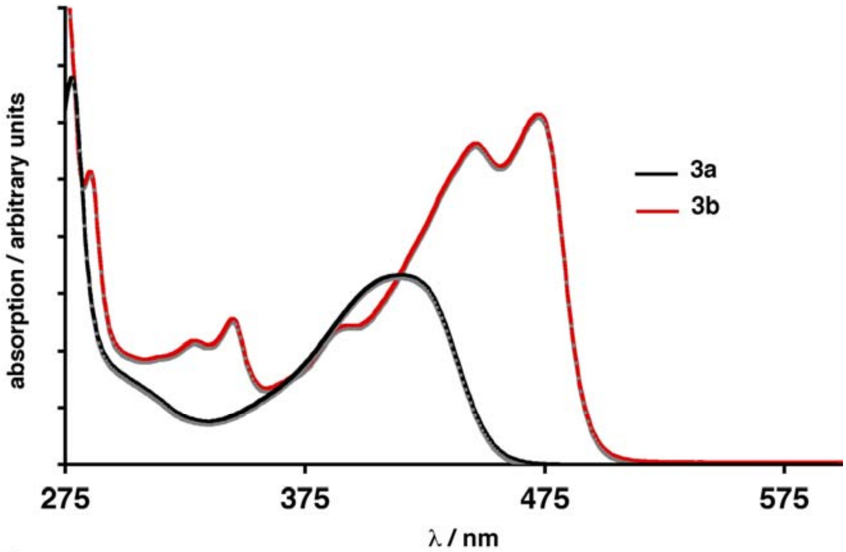


Figure S1. UV-Vis spectra of **3a** and **3b** in THF.

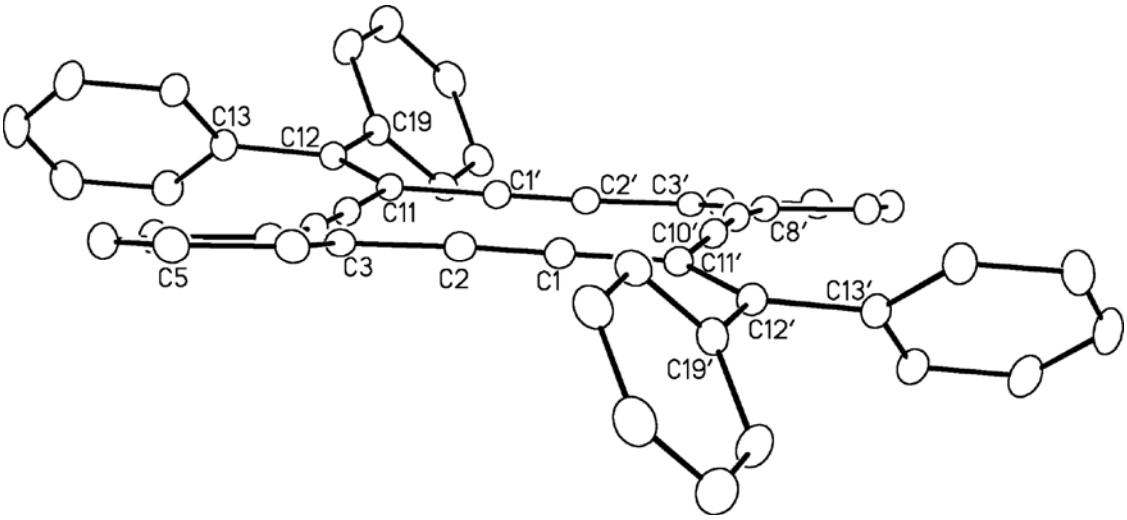


Figure S2. Edge on view of **3a** from X-ray crystallographic analysis.

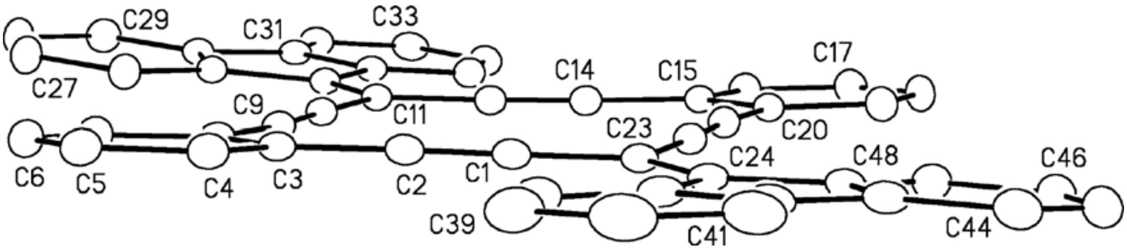


Figure S3. Edge on view of **3b** from X-ray crystallographic analysis.

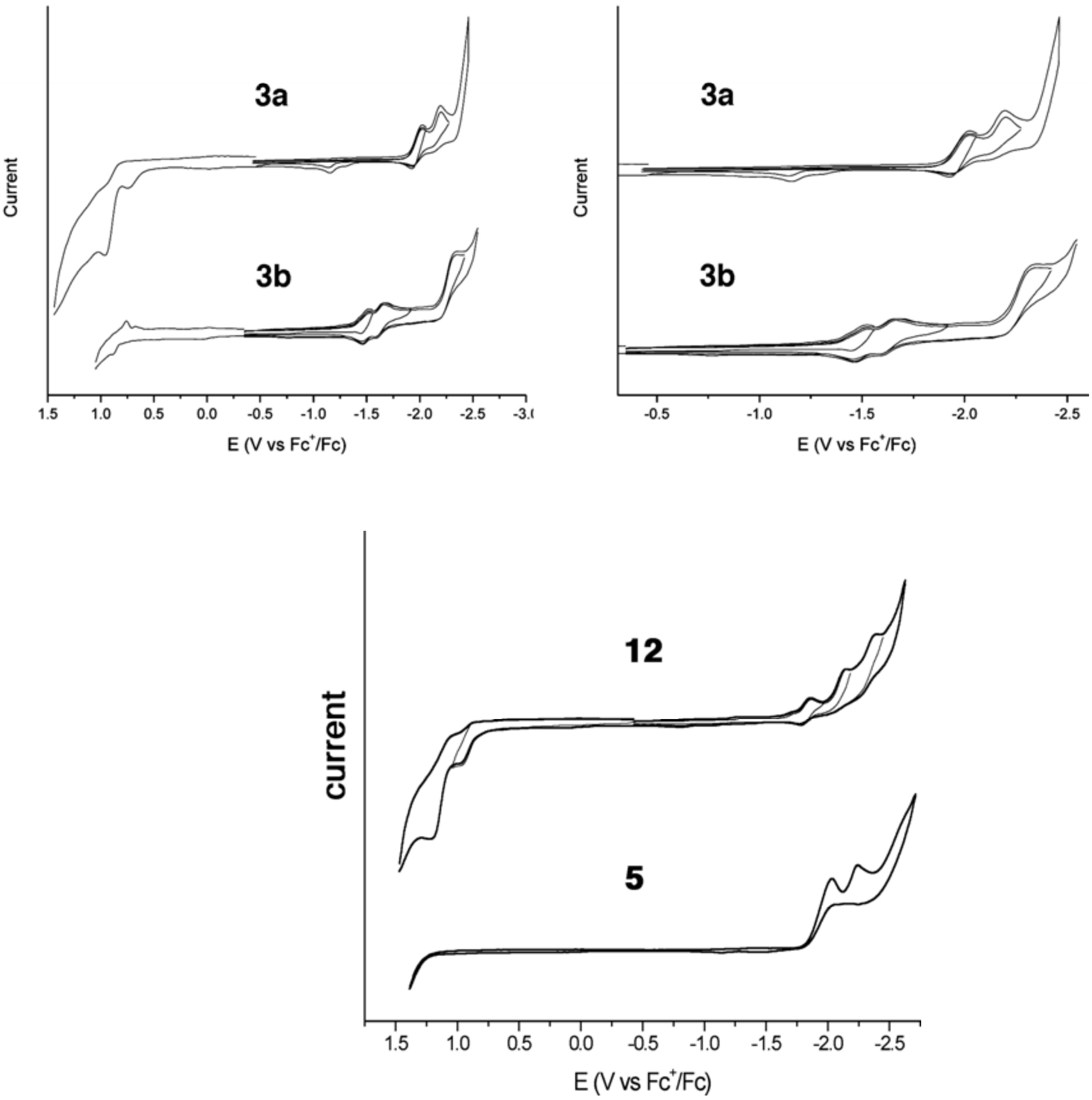


Figure S4. Top right) Cyclic voltammograms of radiaannulenes **3a** and **3b**. Top left) Cathodic section of the CV of radiaannulenes **3a** and **3b**. Bottom) Cyclic voltammograms of enediynes **5** and **12**.

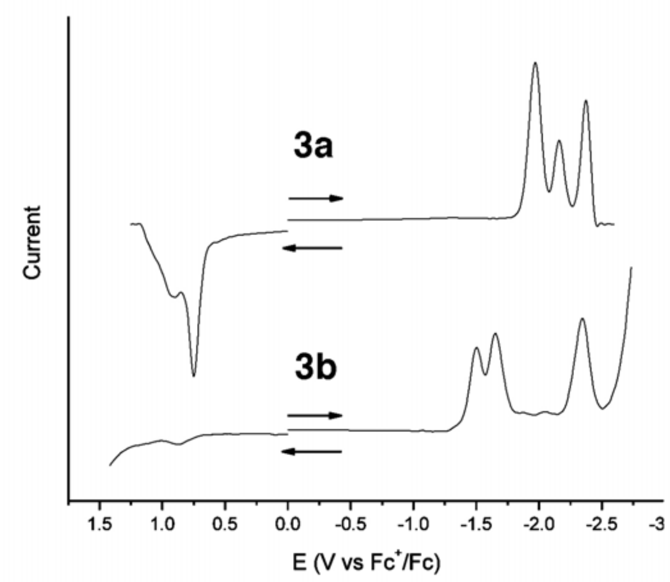


Figure S5. OSWV of radiaannulenes **3a** and **3b**.

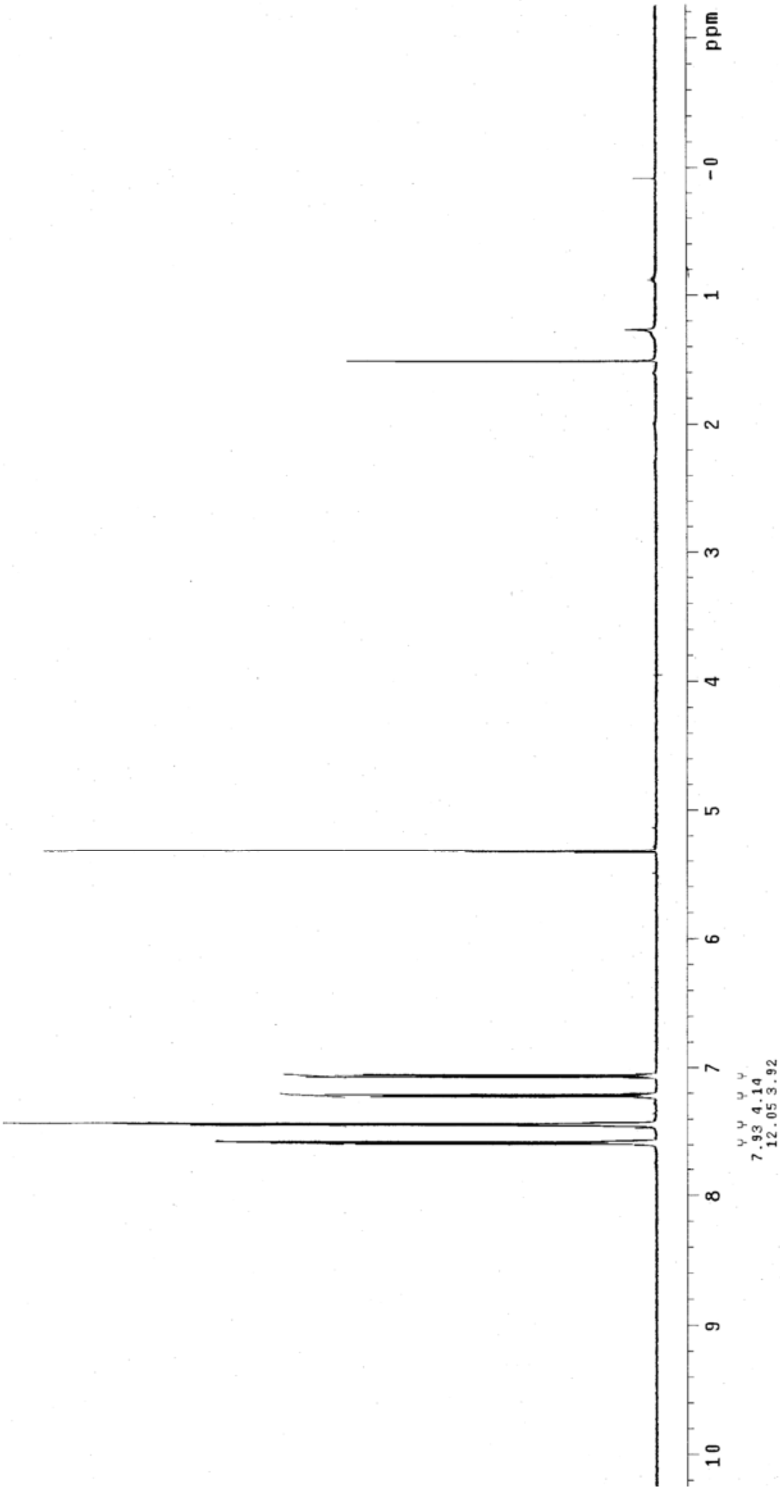


Figure S6. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) for radiaannulene **3a**.

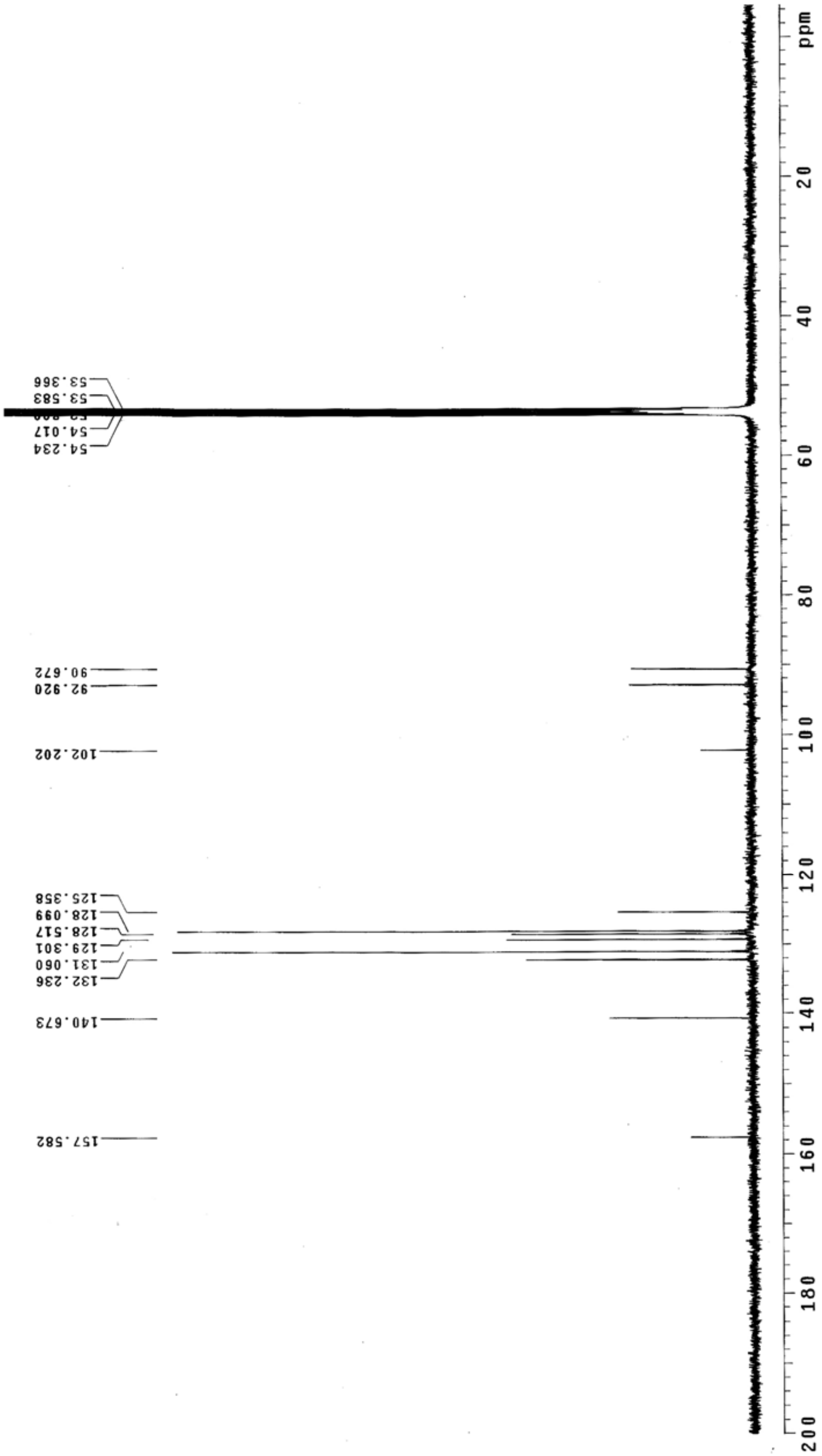


Figure S7. ^{13}C NMR spectrum (125 MHz, CD_2Cl_2) for radiaannulene **3a**.

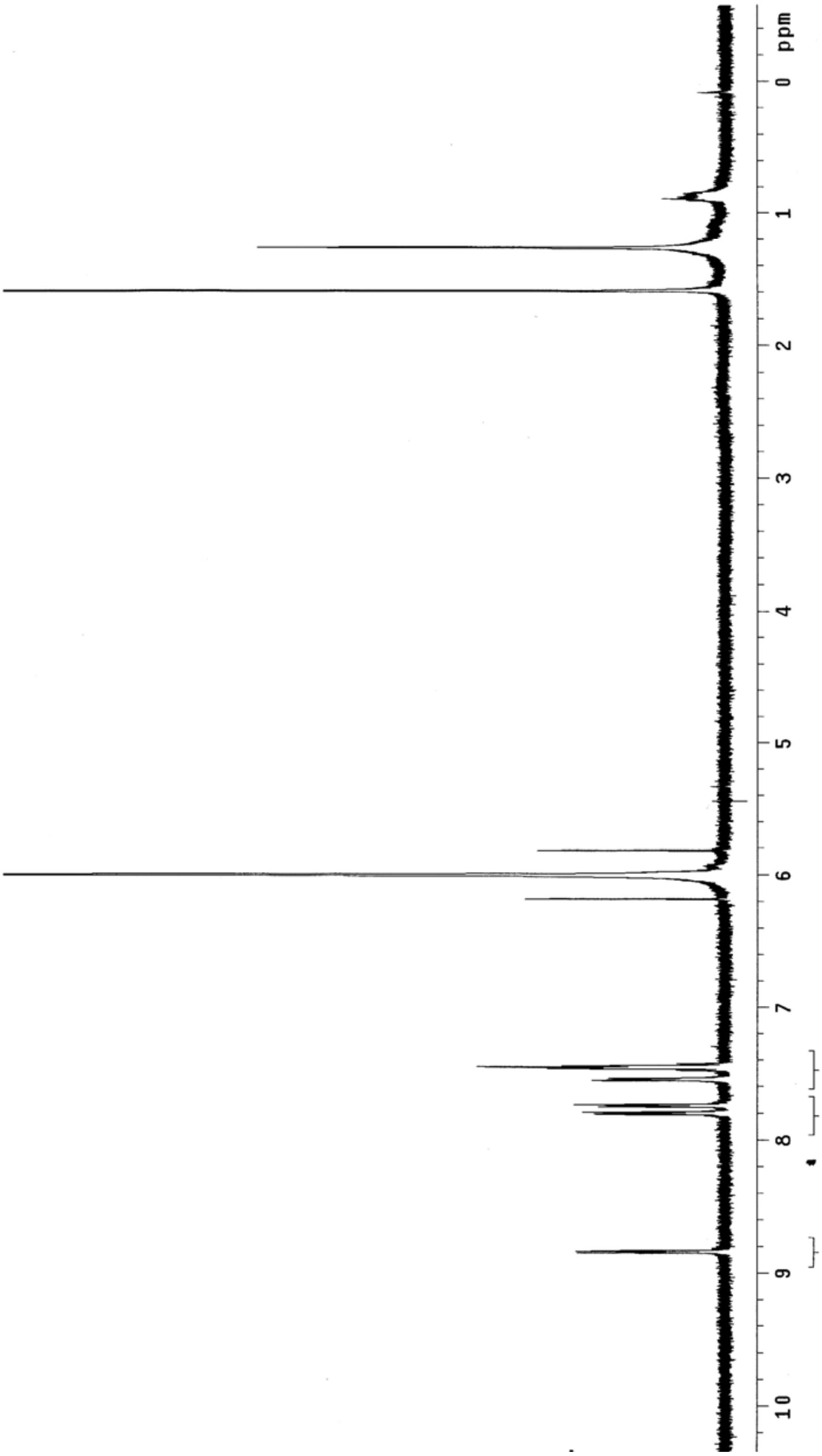


Figure S8. ^{1}H NMR spectrum (500 MHz, $C_2D_2Cl_4$) for radiaannulene **3b**.

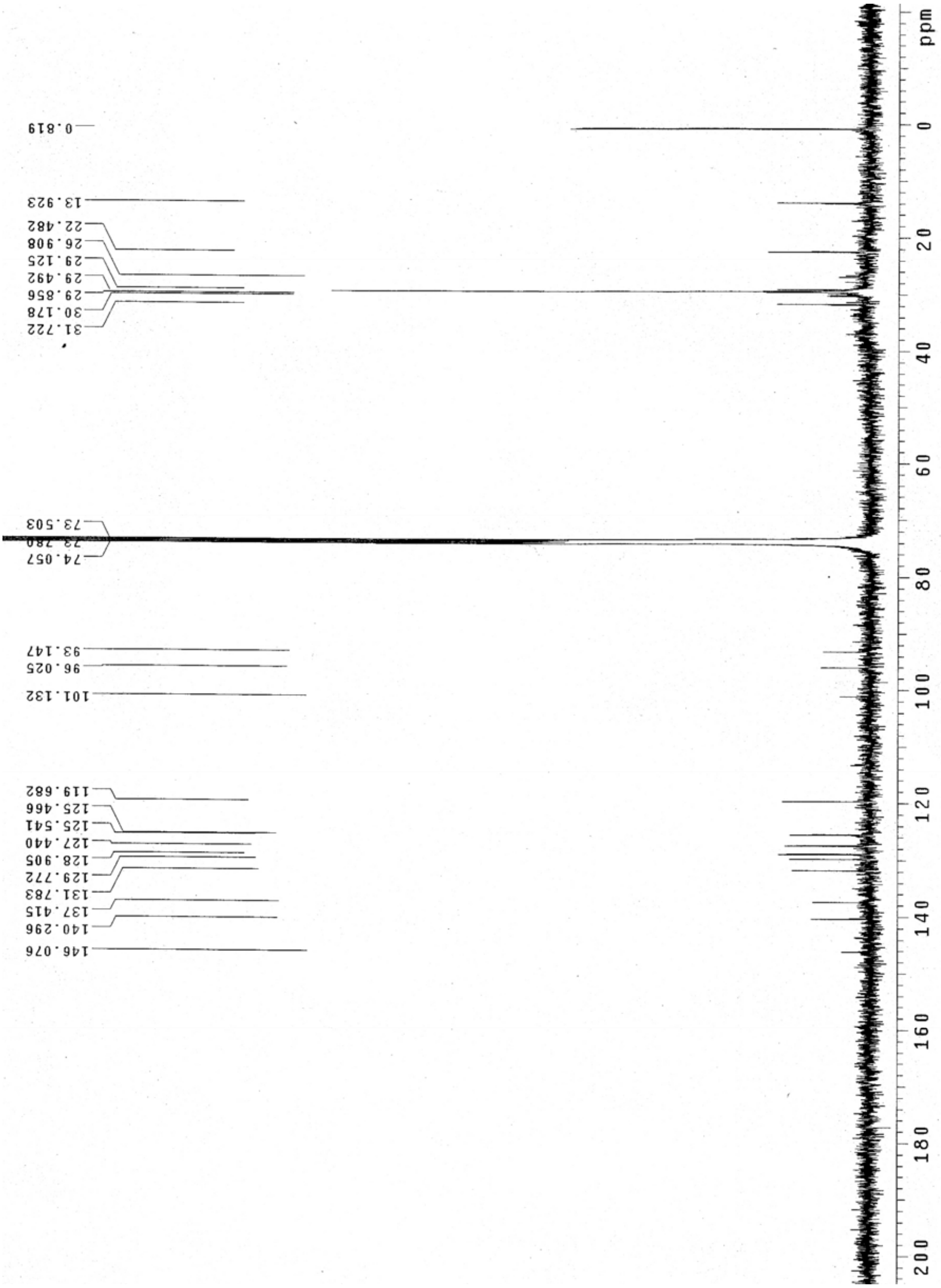


Figure S9. ^{3}C NMR spectrum (125 MHz, $C_2D_2Cl_4$) for radiaannulene **3b**.

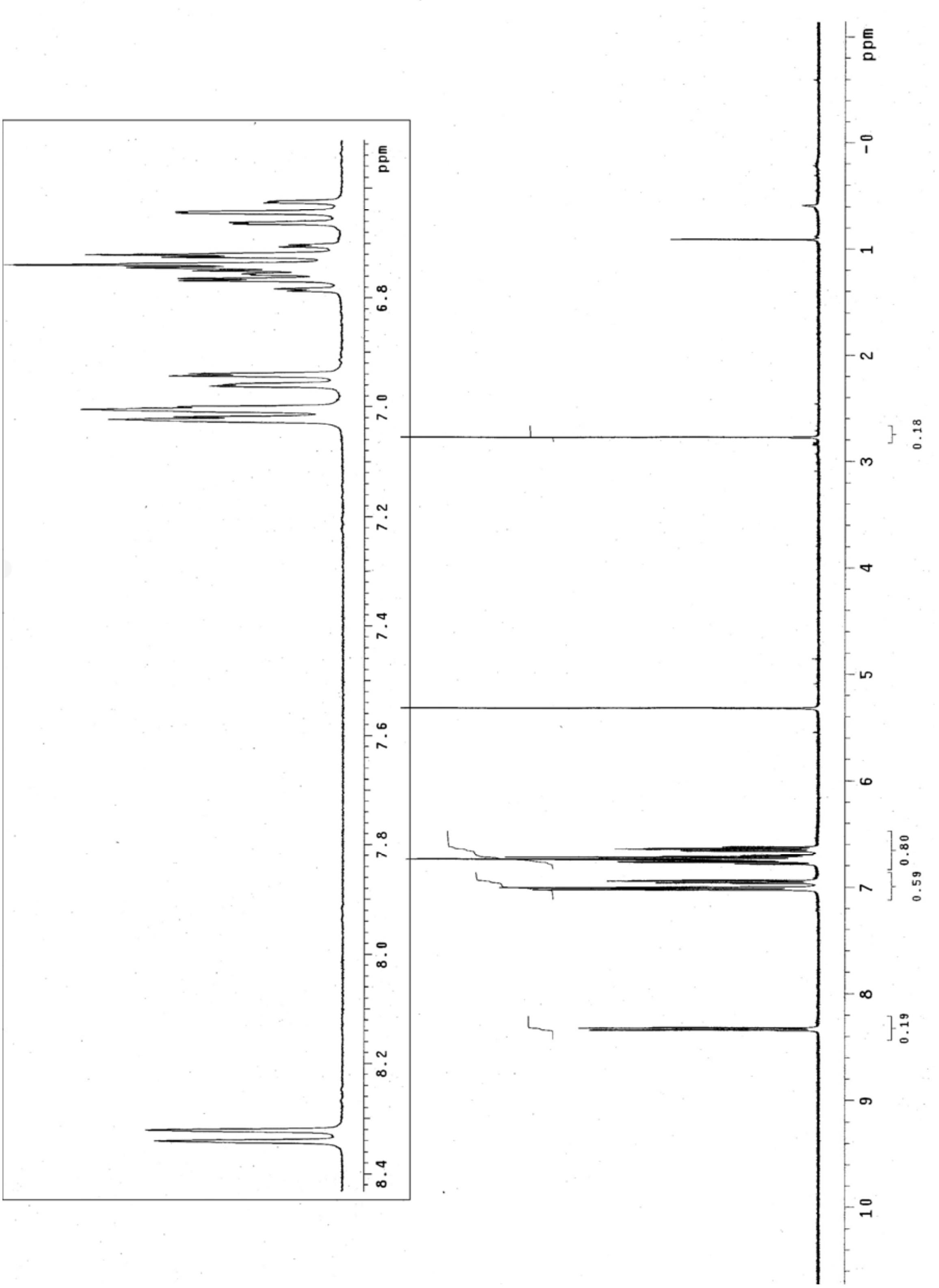


Figure S10. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) for **11**.

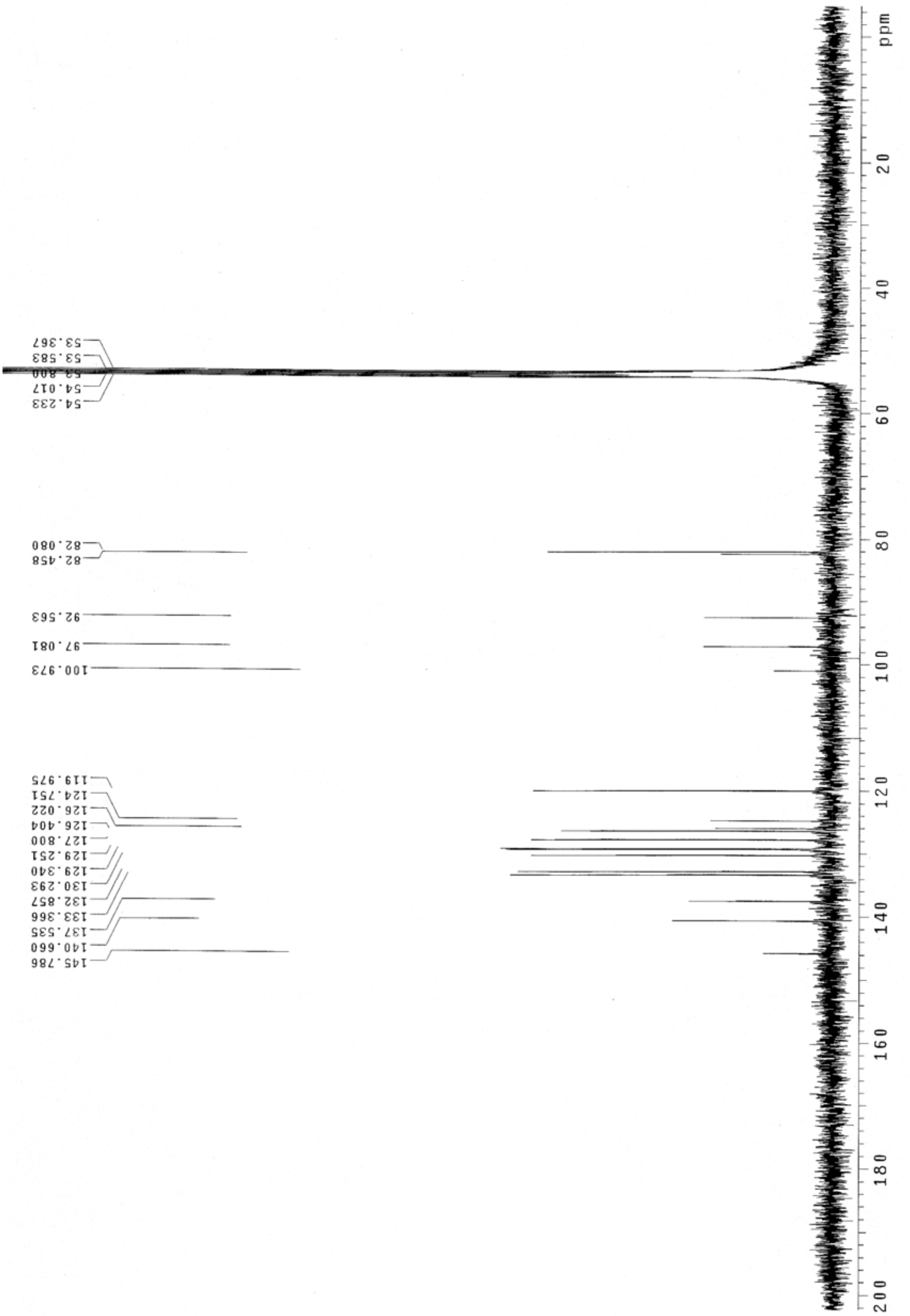


Figure S11. ^{3}C NMR spectrum (125 MHz, CD_2Cl_2) for **11**.

References:

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1. N. Treitel, L. Eshdat, T. Sheradsky, P. M. Donovan, R. R. Tykwinski, L. T. Scott, H. Hopf, and M. Rabinovitz, *J. Am. Chem. Soc.*, 2006, **128**, 4703.
2. G. C. Paul and J. J. Gajewski, *Synthesis* **1997**, 524.
3. M. L. Bell, R. C. Chiechi, C. A. Johnson, D. B. Kimball, A. J. Matzger, W. B. Wan, T. J. R. Weakley, and M. M. Haley, *Tetrahedron*, 2001, **57**, 3507.