



Supporting Information

for

***N*-Arylphenothiazines as strong donors for photoredox catalysis – pushing the frontiers of nucleophilic addition of alcohols to alkenes**

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Beilstein J. Org. Chem. **2019**, *15*, 52–59. doi:10.3762/bjoc.15.5

Copies of ^1H and ^{13}C NMR spectra, mass spectra, absorption and emission spectra and cyclic voltammetry data of 1–11 and 17

Materials and methods

All chemicals were purchased from Sigma Aldrich, Fluka, Alfa Aesar, ABCR or Tokyo Chemical Industry (TCI) and used as received if not otherwise stated. Benchmark experiments for addition of methanol to α -methylstyrene were performed using Fischer HPLC grade solvent.

NMR spectroscopic data were recorded using the following spectrometer hardware. Bruker B-ACS 60, ^1H NMR (300 MHz), ^{13}C NMR (75 MHz); Bruker Avance DRX 400, ^1H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{19}F NMR (376 MHz); Bruker Ascend 500, ^1H NMR (500 MHz), ^{13}C NMR (126 MHz), ^{19}F NMR (470 MHz). Chemical shifts of the ^1H , ^{13}C and ^{19}F NMR spectra are reported in parts per million (ppm) relative to the solvent as an internal standard and converted to the TMS-reference system by applying frequency correction using the values of Fulmer et al. [S1]. Routine ^{13}C NMR spectroscopy was recorded while applying broadband ^1H -decoupling. The chemical shifts of ^{19}F NMR experiments are reported relative to CCl_3F as standard, which was added in a concentration of 0.1% to the neat NMR solvent. Coupling constants (J) are given in hertz (Hz) and the multiplicity of signals is reported as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), p (pentet), sext (sextet), m (multiplet), br. s (broad singlet), dt (doublet of triplets), td (triplet of doublets), dp (doublet of pentets), ddp (doublet of doublet of pentets). Analytical GC determination of the yields of the catalysis was carried out with a Bruker 430 GC instrument equipped with a capillary column FactorFourTM VF-5 ms (30 m \times 0.25 mm \times 0.25 μm), using flame ionization detection. The oven temperature program was: initial temperature 95 $^\circ\text{C}$, hold for 1 min, ramp at 15 $^\circ\text{C}/\text{min}$ to 220 $^\circ\text{C}$, hold for 4 min, ramp at 15 $^\circ\text{C}/\text{min}$ to 325 $^\circ\text{C}$, hold for 2 min. The injector transfer line temperature was set

to 220 °C. Measurements were performed in split–split mode using hydrogen as the carrier gas (flow rate 30 mL/min).

For the calculation of the GC yields a concentration series with (2-methoxypropan-2-yl)benzene (**17**) and 2-bromotoluol (8.77 µmol/mL) as internal standard was prepared. The R-value of the series was determined to be 0.91. To analyze the catalysis mixture, 100 µL of the crude reaction mixture, 174.6 µL of a stock solution of 2-bromotoluol (8.77 µmol/mL) and 724.6 µL ethyl acetate were mixed and shaken vigorously. Then, a volume of 300 µL of the resulting solution was transferred to an GC vial.

Irradiation of the photochemical reactions was carried out using a setup which was designed and manufactured by the University of Regensburg and the workshop of the Institute for Physical Chemistry at KIT Karlsruhe. We warmly thank Dieter Waltz and Klaus Stree for their kind support with manufacturing the irradiation hardware. A Nichia NVSU233A LED was applied for 365 nm irradiation and the photoreactions were irradiated from the bottom. The temperature during the reaction time was controlled using a LAUDA Alpha R8 thermostat. High resolution mass spectrometry was performed on a Finnigan Modell MAT 95 using an electron impact ionization source or on a Q Exactive Plus Orbitrap from Thermo Scientific. MALDI mass spectra were recorded on a Bruker Daltonics Biflex-IV spectrometer, operated in linear negative mode with 3-hydroxy-2-pyridinecarboxylic acid as a matrix. GC–MS coupling was recorded using a Varian 431 GC with a capillary column FactorFour™ VF-5 ms (30 m × 0.25 mm × 0.25 µm) and a Varian 210 ion trap mass detector. Thin layer chromatography was performed using Fluka silica gel 60 F254 coated aluminium foil. Flash chromatography was carried out on silica gel 60 supplied by Sigma Aldrich (43–60 µm. Spectroelectrochemical measurements were carried out using a Varian Cary 50 spectrometer at room temperature and a HORBIA-Scientific

Fluoromax-4 spectrofluorometer with an AC 200 thermostat from Thermo Scientific and the FluoroEssence software V3.5 in semi-micro quartz glass cuvettes (width 1 cm, volume 1.4 mL) from Starna.

The cyclic voltammetry measurements were carried out with complete exclusion of air and moisture. We warmly thank Prof. Dr. Frank Breher for sharing his CV infrastructure. The working electrode and the counter electrode were made of platinum. Reference electrode serving as the potential zero point was made of silver. For the electrolysis solution, a 0.05 M solution of tetrabutylammonium hexafluorophosphate in dry DCM or in dry MeCN was prepared.

Photochemical experiment setup

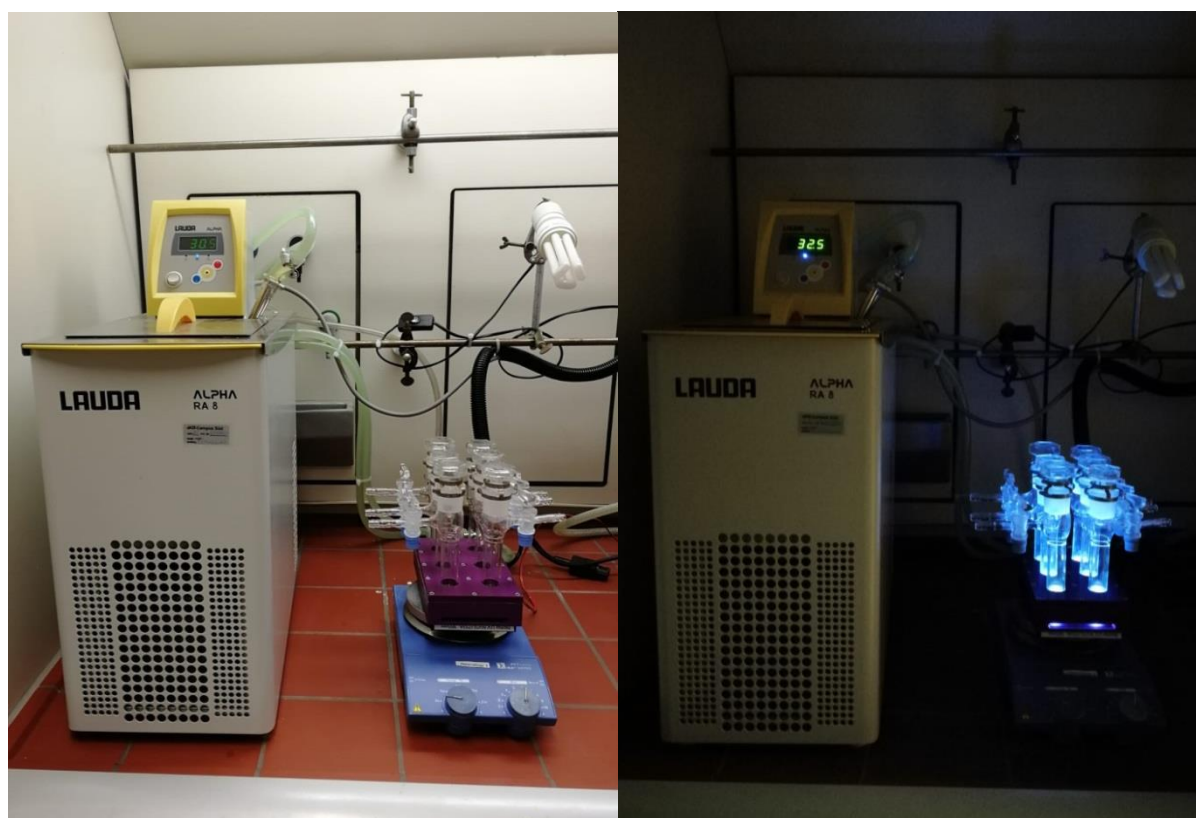
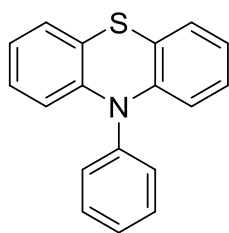


Figure S1: Modular LED irradiation setup and cooling blocks.

Synthetic procedures

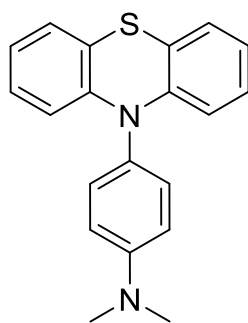
General procedure A - synthesis of *N*-phenylphenothiazines. *N*-phenylphenothiazines were synthesized similarly to the reported procedure [S2]. Phenothiazine (1.00 equiv) was dissolved in anhydrous toluene (0.51 M). Bromobenzene (1.22 equiv), KO*t*-Bu (1.29 equiv) and (*t*-Bu)₃PHBF₄ (6 mol %) were added, followed by Pd₂dba₃ (3 mol % as 6 mol % Pd). The reaction mixture was degassed using three freeze-pump-thaw cycles and finally stirred under reflux for 20 °h. After reaching room temperature, 100 mL EtOAc and 50 mL water were added to the reaction mixture. After phase separation, the aqueous phase was extracted additionally with 3 × 100 mL EtOAc. The combined organic phases were dried over Na₂SO₄, the solvent evaporated and the crude product purified by column chromatography.

General procedure B - synthesis of *N*-phenylphenothiazines. *N*-Phenothiazine (1.00 equiv), aryl halide (1.50 equiv), sodium *tert*-butoxide (2.50 equiv), Pd₂dba₃ (0.05 equiv/5 mol %) and tricyclohexylphosphine (0.07 equiv) were dissolved in anhydrous toluene (0.26 M). The reaction mixture was then stirred under reflux under inert atmosphere overnight. The reaction mixture was cooled to room temperature and 50 mL water were added. The reaction mixture was extracted with EtOAc (3 × 100 mL). The combined organic phases were dried over MgSO₄, the solvent removed and the crude product purified by column chromatography.



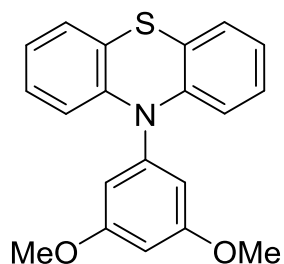
Synthesis of 1

10-Phenyl-10*H*-phenothiazine was synthesized similarly to the reported procedure [S2]. Phenothiazine (810 mg, 4.06 mmol, 1.00 equiv), bromobenzene (520 μ L, 780 mg, 4.97 mmol, 1.22 equiv), KO*t*-Bu (587 mg, 5.23 mmol, 1.29 equiv), (*t*-Bu)₃PHBF₄ (71 mg, 0.244 mmol, 6 mol %) and Pd₂dba₃ (112 mg, 0.122 mmol, 6 mol % Pd) were used for the preparation following general procedure A and purified by column chromatography (cyclohexane, silica gel, *R*_f = 0.33). The product was obtained as colorless solid (1.08 g, 3.93 mmol, 97%) and analytical data were identical with those in the literature [S3].



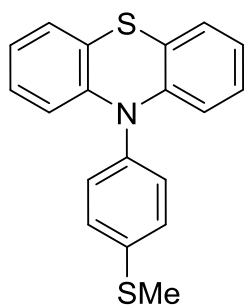
Synthesis of 2

Phenothiazine (750 mg, 3.80 mmol, 1.00 equiv), 4-bromo-*N,N*-dimethylaniline (1.14 g, 5.70 mmol, 1.50 equiv), NaO*t*-Bu (913 mg, 9.50 mmol, 2.50 equiv), tricyclohexylphosphine (73 mg, 0.26 mmol, 0.07 equiv) and Pd₂dba₃ (173 mg, 0.19 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane/CH₂Cl₂ 4:1, silica gel, *R*_f = 0.14). The product was obtained as white solid (229.9 mg, 0.722 mmol, 19%): ¹H NMR (300 MHz, THF-*d*₈): δ (ppm) = 7.17 (d, *J* = 8.7 Hz, 2H), 6.95 - 6.89 (m, 4H), 6.80 - 6.68 (m, 4H), 6.22 (d, *J* = 8.1 Hz, 2H), 3.03 (s, 6H): ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 150.3, 145.4, 131.9, 129.4, 127.2, 126.9, 122.4, 119.8, 116.1, 114.1, 40.6. MALDI-TOF-MS: *m/z* (%) = 318.7 [*M*⁺].



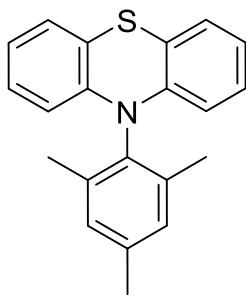
Synthesis of 3

Phenothiazine (750 mg, 3.80 mmol, 1.00 equiv), bromodimethoxybenzene (1.24 g, 5.70 mmol, 1.50 equiv), NaOt-Bu (910 mg, 9.50 mmol, 2.50 equiv), tricyclohexylphosphine (75 mg, 0.26 mmol, 0.07 equiv) and Pd₂dba₃ (170 mg, 0.19 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane/CH₂Cl₂ 5:1, silica gel, *R*_f = 0.19). The product was isolated as light yellow powder (1.08 g, 3.22 mmol, 85%): ¹H NMR (300 MHz, THF-d₈): δ (ppm) = 6.96 (d, *J* = 7.4 Hz, 2H), 6.86 – 6.74 (m, 4H), 6.61 (s, 1H), 6.57 (s, 6H), 6.33 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 162.5, 143.9, 127.1, 126.8, 122.7, 120.3, 116.3, 108.0, 105.5, 100.5, 55.6. MALDI-TOF-MS : *m/z* (%) = 335.9 [M⁺].



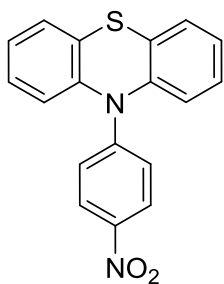
Synthesis of 4

Phenothiazine (1.00 g, 5.00 mmol, 1.00 equiv), 4-bromothioanisole (2.20 mL, 1.50 g, 7.50 mmol, 1.50 equiv), NaOt-Bu (1.20 g, 12.5 mmol, 2.50 equiv), tricyclohexylphosphine (100 mg, 0.35 mmol, 0.07 equiv) and Pd₂dba₃ (230 mg, 0.25 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane/CH₂Cl₂ 5:1, silica gel, *R_f* = 0.20). The product was isolated as colorless powder (1.44 g, 4.48 mmol, 90%): ¹H NMR (500 MHz, THF-d₈): δ (ppm) = 7.50 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.86 – 6.72 (m, 4H), 6.22 (d, *J* = 7.3 Hz, 2H), 2.55 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 139.0, 137.6, 135.2, 131.6, 128.2, 127.6, 127.2, 126.9, 116.0, 15.7. MALDI-TOF-MS: *m/z* (%) = 319.8 [M⁺].



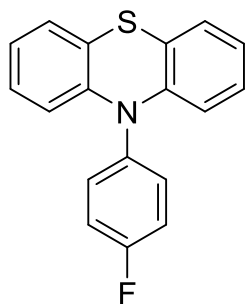
Synthesis of 5

Phenothiazine (750 mg, 3.80 mmol, 1.00 equiv), 2-bromomesitylene (0.870 mL, 1.13 g, 5.70 mmol, 1.50 equiv), NaOt-Bu (910 mg, 9.50 mmol, 2.50 equiv), tricyclohexylphosphine (75 mg, 0.26 mmol, 0.07 equiv) and Pd₂dba₃ (170 mg, 0.19 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane, silica gel, *R_f* = 0.20). The product was obtained as colorless solid (340 mg, 0.874 mmol, 23%): ¹H NMR (300 MHz, THF-d₈): δ (ppm) = 7.10 (s, 2H), 6.85 (d, *J* = 7.0 Hz, 2H), 6.75 – 6.65 (m, 4H), 2.35 (s, 3H), 2.13 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 141.2, 138.0, 134.6, 130.1, 128.7, 127.0, 126.2, 121.8, 118.2, 113.8, 21.0, 17.9. MALDI-TOF-MS: *m/z* (%) = 317.1 [M⁺].



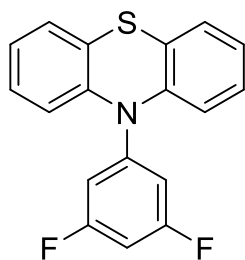
Synthesis of 6

[S4]. Phenothiazine (829 mg, 4.16 mmol, 1.00 equiv), 4-bromonitrobenzene (1.26 g, 6.24 mmol, 1.50 equiv), NaOt-Bu (1.00 g, 10.4 mmol, 2.50 equiv), tricyclohexylphosphine (82.0 mg, 0.29 mmol, 0.07 equiv) and Pd₂dba₃ (192 mg, 0.21 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane/CH₂Cl₂ 2:1, silica gel, *R*_f = 0.14). The product was isolated as yellow powder (595 mg, 1.86 mmol, 45%): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.05 (d, *J* = 9.3 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 9.3 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 151.2, 141.1, 140.6, 134.8, 129.3, 127.7, 127.2, 126.9, 125.7, 113.9. HR-EI-MS *m/z* (calc.) = 320.0619 [M⁺]; *m/z* (found) = 321.0689 [M+H⁺].



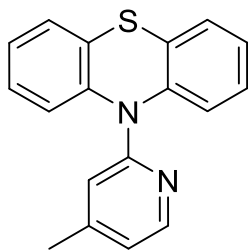
Synthesis of 7

Phenothiazine (810 mg, 4.06 mmol, 1.00 equiv), 1-bromo-4-fluorobenzene (875 mg, 549 μ L, 4.97 mmol, 1.22 equiv), KO t -Bu (587 mg, 5.23 mmol, 1.29 equiv), (t -Bu)₃PHBF₄ (71 mg, 0.244 mmol, 6 mol %) and Pd₂dba₃ (112 mg, 0.122 mmol, 6 mol % Pd) were used for the preparation following general procedure A and purified by column chromatography (cyclohexane, silica gel, R_f = 0.40). The product was obtained as colorless solid (1.10 g, 3.75 mmol, 92%): ¹H NMR (acetonitrile-*d*₃, 300 MHz): δ 7.49 – 7.32 (m, 4H), 7.04 (dd, J = 7.6, 1.7 Hz, 2H), 6.91 (ddd, J = 8.4, 7.4, 1.7 Hz, 2H), 6.84 (td, J = 7.4, 1.3 Hz, 2H), 6.20 (dd, J = 8.2, 1.3 Hz, 2H); ¹³C NMR (126 MHz, acetonitrile-*d*₃) δ 163.1 (d, J = 245.8 Hz), 145.1, 137.9 (d, J = 3.1 Hz), 133.8 (d, J = 8.9 Hz), 128.2, 127.6, 123.7, 120.8, 118.7 (d, J = 22.8 Hz), 117.0. ¹⁹F NMR (471 MHz, acetonitrile-*d*₃) δ -113.3 – -113.4 (m, 1F). HR-ESI-MS m/z (calc.) = 293.0674 [M^+]; m/z (found) = 293.0676 [M^+].



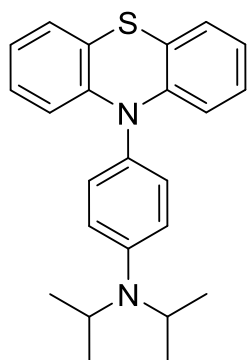
Synthesis of 8

Phenothiazine (810 mg, 4.06 mmol, 1.00 equiv), 1-bromo-3,5-difluorobenzene (575 μ L, 964 mg, 4.97 mmol, 1.22 equiv), KO t -Bu (587 mg, 5.23 mmol, 1.29 equiv), (t -Bu) $_3$ PHBF $_4$ (71 mg, 0.244 mmol, 6 mol %) and Pd $_2$ dba $_3$ (112 mg, 0.122 mmol, 6 mol % Pd) were used for the preparation following general procedure A. The product was obtained as colorless solid (976 mg, 3.13 mmol, 77%): ^1H NMR (500 MHz, acetonitrile- d_3): δ 7.32 (dd, J = 7.7, 1.5 Hz, 2H), 7.21 (td, J = 7.8, 1.5 Hz, 2H), 7.11 (td, J = 7.6, 1.4 Hz, 2H), 6.96 (dd, J = 8.1, 1.3 Hz, 2H), 6.81 – 6.69 (m, 3H): ^{13}C NMR (126 MHz, acetonitrile- d_3) δ 165.00 (dd, J = 245.8, 15.4 Hz), 147.64 (t, J = 12.6 Hz), 142.95, 128.8, 128.7, 128.5, 126.03, 123.29, 106.3-106.1 (m), 100.25 (t, J = 26.3 Hz). ^{19}F NMR (471 MHz, acetonitrile- d_3) δ -108.36 – -108.69 (m, 2F). HR-EI-MS: m/z (calc.) = 311.0580 [M^+]; m/z (found) = 311.0579 [M^+].



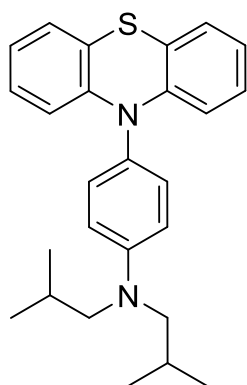
Synthesis of 9

Phenothiazine (750 mg, 3.80 mmol, 1.00 equiv), 2-bromo-4-methylpyridine (0.64 mL, 981 mg, 5.70 mmol, 1.50 equiv), NaO*t*-Bu (910 mg, 9.50 mmol, 2.50 equiv), tricyclohexylphosphine (75 mg, 0.26 mmol, 0.07 equiv) and Pd₂dba₃ (170 mg, 0.19 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane/CH₂Cl₂ 1:1, silica gel, *R*_f = 0.20). The product was isolated as colorless powder (939 mg, 3.23 mmol, 86%): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.20 (d, *J* = 5.1 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.79 (s, 1H), 6.76 (d, *J* = 5.1 Hz, 1H), 2.24 (s, 3H): ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 156.5, 149.4, 147.9, 141.8, 131.6, 128.1, 127.0, 125.9, 125.4, 119.1, 112.4, 21.4. MALDI-TOF-MS : *m/z* (%) = 290.9 [M⁺].



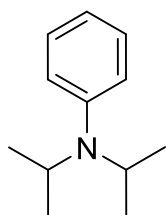
Synthesis of 10

Phenothiazine (518 mg, 2.60 mmol, 1.00 equiv), 4-bromo-*N,N*-diisopropylaniline (**19**, 0.71 mL, 1.00 g, 3.90 mmol, 1.50 equiv), NaO*t*-Bu (625 mg, 6.50 mmol, 2.50 equiv), tricyclohexylphosphine (51.0 mg, 0.18 mmol, 0.07 equiv) and Pd₂dba₃ (119 mg, 0.13 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane/ethylacetate 50:1, silica gel, *R*_f = 0.33). The product was isolated as colorless powder (740 mg, 1.98 mmol, 76%): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.15 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.85 (t, *J* = 6.8 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 2H), 6.30 (d, *J* = 8.0 Hz, 2H), 3.89 (m, 2H), 1.32 (d, *J* = 7.5 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 148.0, 145.2, 131.1, 129.5, 126.9, 126.6, 122.0, 119.6, 118.6, 115.9. MALDI-TOF-MS : *m/z* (%) = 372.90 [M⁺].



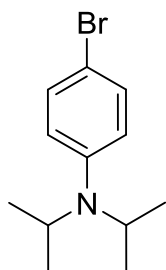
Synthesis of 11

Phenothiazine (795 mg, 3.99 mmol, 1.00 equiv), 4-bromo-*N,N*-diisobutylaniline (**20**, 1.70 g, 5.98 mmol, 1.50 equiv), NaO*t*-Bu (959 mg, 9.98 mmol, 2.50 equiv), tricyclohexylphosphine (78.5 mg, 0.28 mmol, 0.07 equiv) and Pd₂dba₃ (183 mg, 0.20 mmol, 0.05 equiv) were used for the preparation following general procedure B and purified by column chromatography (hexane, silica gel, *R*_f = 0.23). The product was isolated as colorless powder (853 mg, 2.12 mmol, 57%): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.13 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 2H), 6.27 (d, *J* = 8.0 Hz, 2H), 3.21 (d, *J* = 7.0 Hz, 4H), 2.20 – 2.12 (hept, *J* = 6.7 Hz, 2H), 0.96 (d, *J* = 6.7 Hz, 12H): ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 147.9, 145.3, 131.5, 127.9, 126.9, 126.6, 122.0, 119.5, 115.9, 113.7, 60.7, 26.5, 20.5. HR-EI-MS: *m/z* (calc.) = 402.2130 [M⁺]; *m/z* (found) = 402.2120 [M⁺].



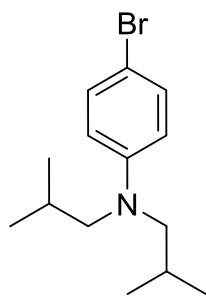
Synthesis of 18

[S5]. A mixture of bromobenzene (3.40 mL, 4.71 g, 30.0 mmol), potassium *tert*-butoxide (5.05 g, 45.0 mmol, 1.50 equiv), diisopropylamine (6.30 mL, 4.55 g, 45 mmol, 1.50 equiv), Pd(dppf)Cl₂ (50 mg, 68.3 μmol, 0.002 equiv) and 40 mL DMSO was degassed (× 3) and heated to 150 °C for 24 h. After cooling to room temperature, the mixture was poured into brine solution (100 mL), then extracted with diethyl ether (2 × 100 mL). The organic layer was separated, dried over MgSO₄ and evaporated. The brown colored residue was suspended into hexanes (100 mL) and extracted with 5% aqueous HCl solution (2 × 100 mL). The aqueous layer was made basic by adding NaOH pellets at 0 °C, then extracted with diethyl ether (2 × 100 mL). The separated organic layer was dried over MgSO₄ and evaporated to yield an orange oil (1.12 g, 6.32 mmol, 21%): ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.20 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 3.77 (hept, *J* = 6.6 Hz, 2H), 1.21 (d, *J* = 6.6 Hz, 12H). HR-ESI-MS: *m/z* (calc.) = 177.1517 [M⁺]; *m/z* (found) = 178.1588 [M+H⁺].



Synthesis of 19

[S5]. To a solution of **18** (1.10 mL, 1.00 g, 5.64 mmol, 1.00 equiv) in 15 mL of DMF at $-10\text{ }^{\circ}\text{C}$ was added dropwise a solution of NBS (1.05 g, 5.92 mmol, 1.05 equiv) in 10 mL of DMF. The mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 1 h. The mixture was diluted with brine (100 mL) and extracted with ethyl acetate ($3 \times 100\text{ mL}$). The combined organic layers were dried over MgSO_4 and evaporated. The residue was redissolved into diethyl ether (75 mL) and filtered. The filtrate was washed with NaOH (3 M, 100 mL) and dried over MgSO_4 . The solvent was removed to give a yellow oil (1.34 g, 5.25 mmol, 93%): ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 7.25 (d, $J = 8.8\text{ Hz}$, 2H), 6.74 (d, $J = 9.1\text{ Hz}$, 2H), 3.73 (hept, $J = 6.7\text{ Hz}$, 2H), 1.19 (d, $J = 6.9\text{ Hz}$, 12H).



Synthesis of 20

[S5]. To a solution of *N,N*-diisobutylaniline (1.67 mL, 1.50 g, 7.30 mmol, 1.00 equiv) in 20 mL of DMF at $-10\text{ }^{\circ}\text{C}$ was added dropwise a solution of NBS (1.37 g, 7.67 mmol, 1.05 equiv) in 10 mL of DMF. The mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 40 min. The mixture was diluted with brine (100 mL) and extracted with ethyl acetate ($3 \times 100\text{ mL}$). The combined organic layers were dried over MgSO_4 and evaporated. The residue was redissolved into diethyl ether (75 mL) and filtered. The filtrate was washed with NaOH (3 M, 100 mL) and dried over MgSO_4 . The solvent was removed to give a light yellow powder (1.91 g, 6.72 mmol, 92%): ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 7.24 (d, $J = 8.7\text{ Hz}$, 2H), 6.50 (d, $J = 8.7\text{ Hz}$, 2H), 3.11 (d, $J = 7.5\text{ Hz}$, 4H), 2.04 (hept, $J = 6.7\text{ Hz}$, 2H), 0.88 (d, $J = 6.7\text{ Hz}$, 12H): ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) = 147.2, 131.8, 114.2, 106.9, 60.5, 26.4, 20.4. HR-EI-MS: m/z (calc.) = 283.0936 [M^+]; m/z (found) = 284.1003 [$\text{M}+\text{H}^+$].

Spectroscopic data

UV-vis absorption

The UV-vis absorption spectra were recorded at 20 °C in acetonitrile (HPLC grade, Fisher Scientific) or dichloromethane (HPLC grade, Fisher Scientific) using slit 2 nm.

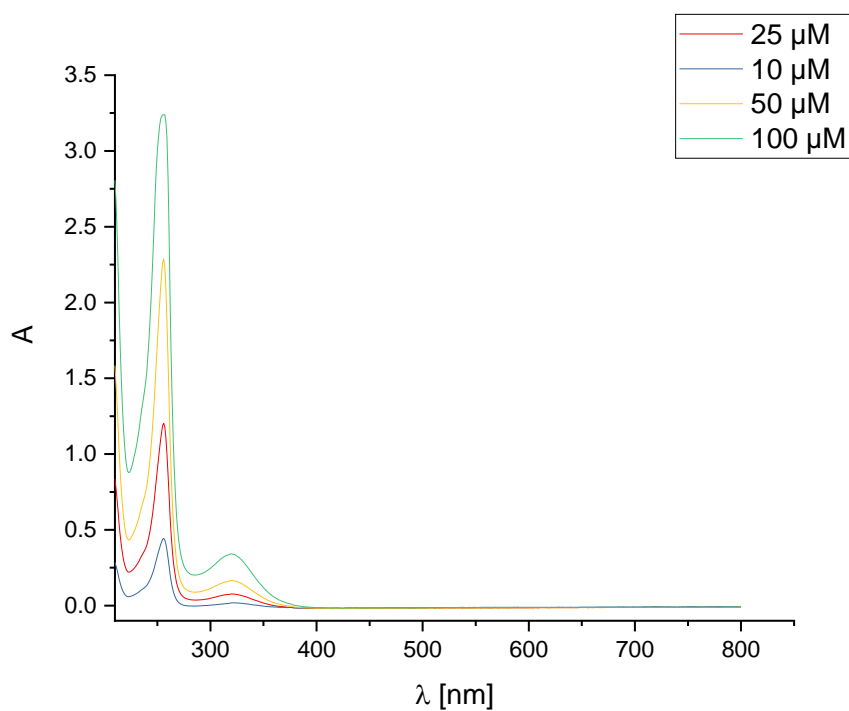


Figure S2: UV-vis absorption spectrum of **1** in MeCN.

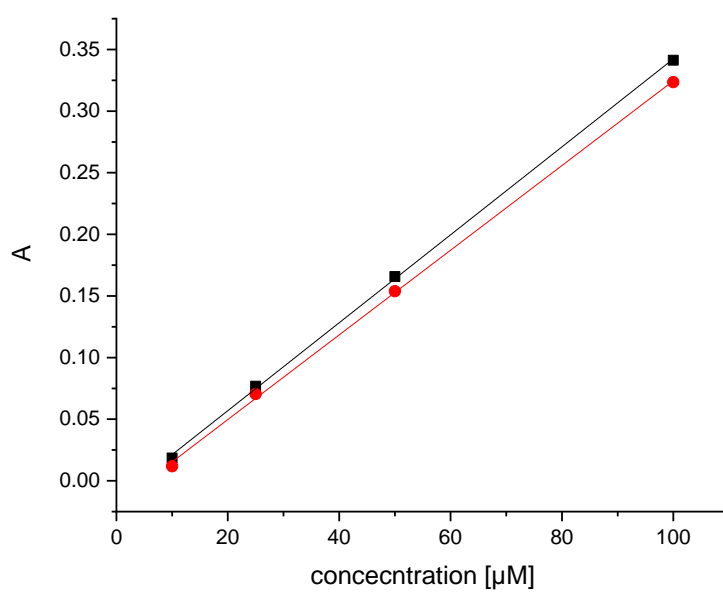


Figure S3: Concentration-dependent UV-vis absorption at 313 nm and 320 nm for determination of the extinction coefficient of 10-phenyl-10*H*-phenothiazine (**1**) in MeCN.

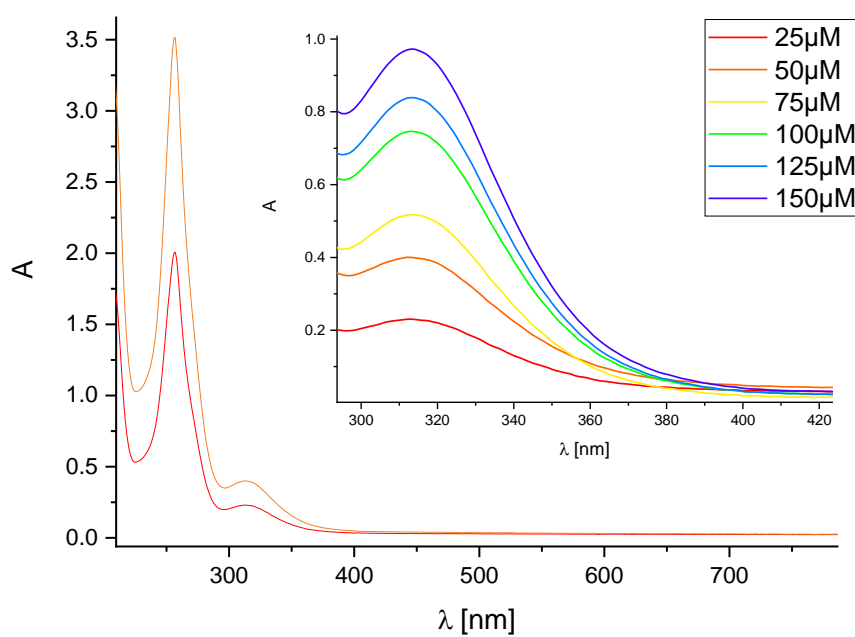


Figure S4: UV-vis absorption spectra of **2** in CH_2Cl_2 .

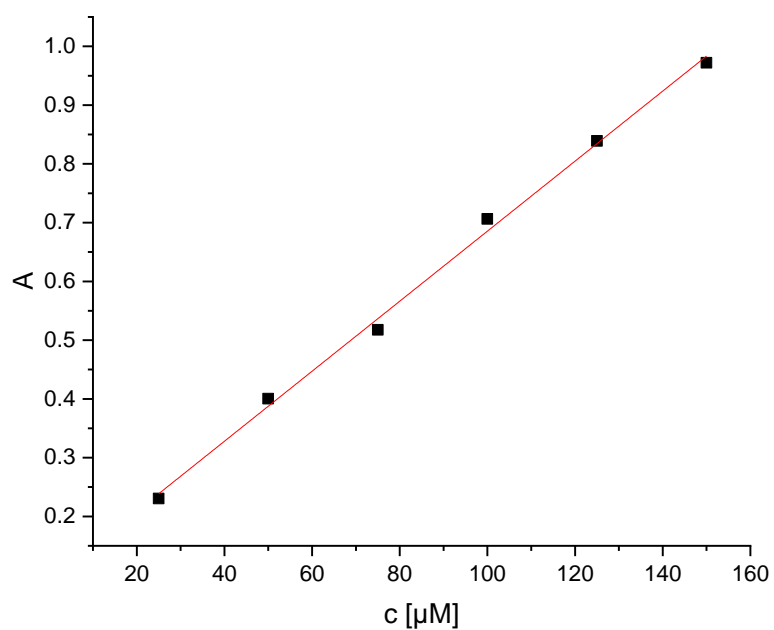


Figure S5: Concentration-dependent UV-vis absorption for determination of extinction coefficient of **2** in CH_2Cl_2 .

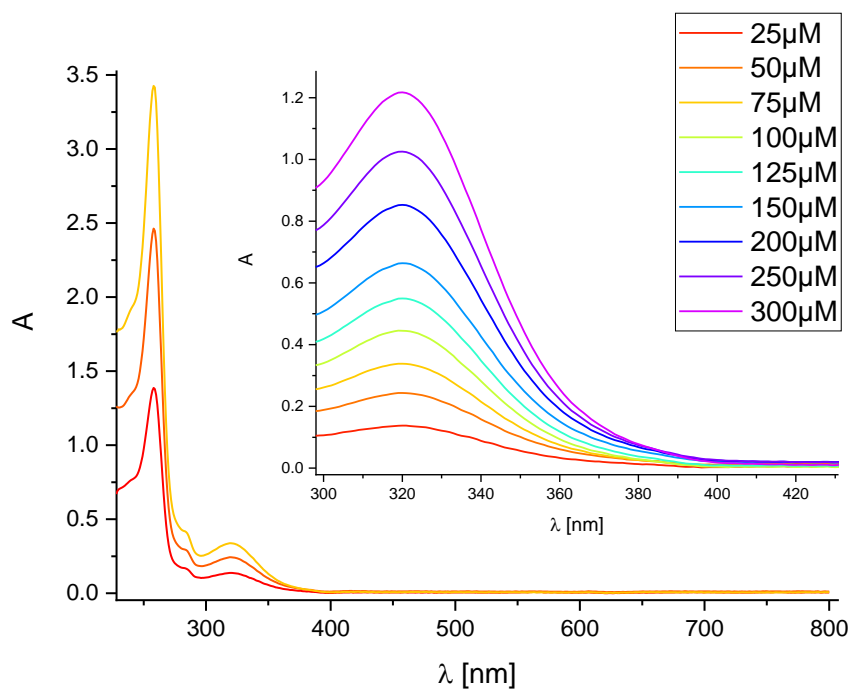


Figure S6: UV-vis absorption spectra of **3** in CH_2Cl_2 .

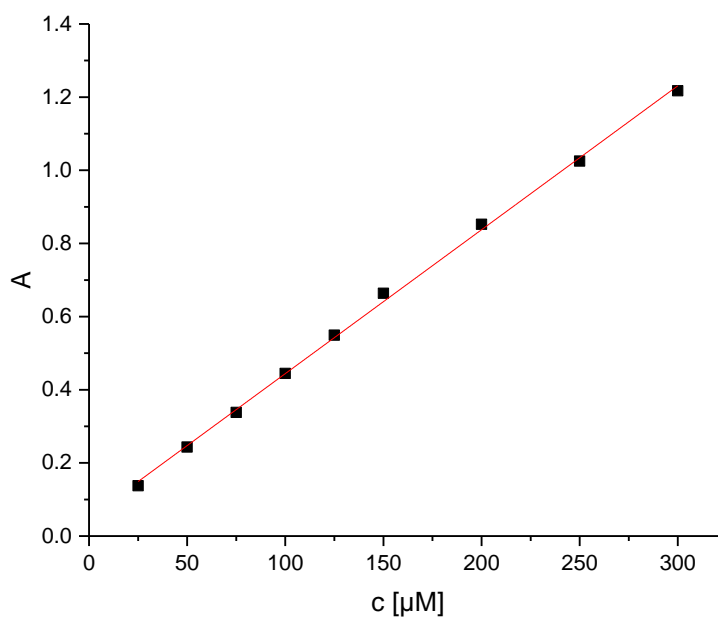


Figure S7: Concentration-dependent UV-vis absorption for determination of extinction coefficient **3** in CH_2Cl_2 .

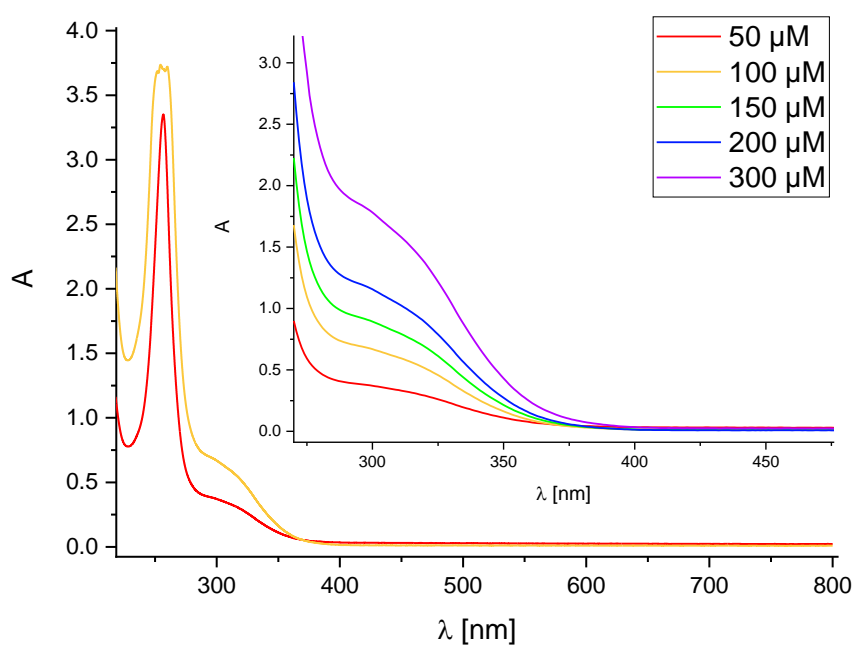


Figure S8: UV-vis absorption spectra of **4** in CH_2Cl_2 .

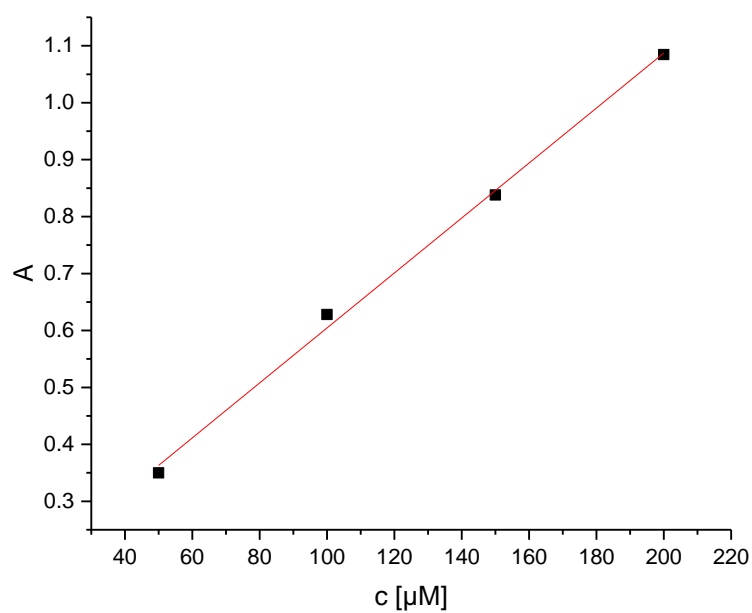


Figure S9: Concentration-dependent UV-vis absorption for determination of extinction coefficient of **4** in CH_2Cl_2 .

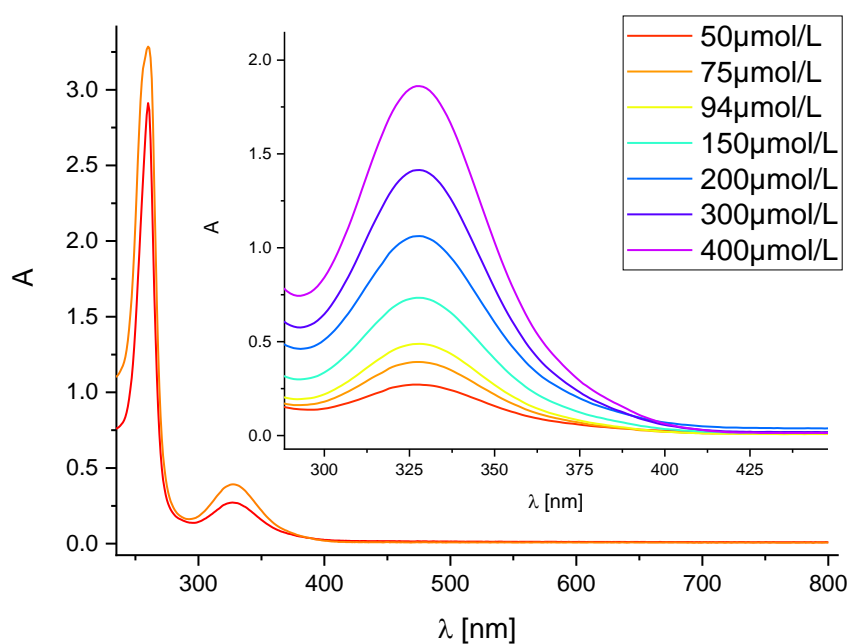


Figure S10: UV-vis absorption spectra of **5** in CH_2Cl_2 .

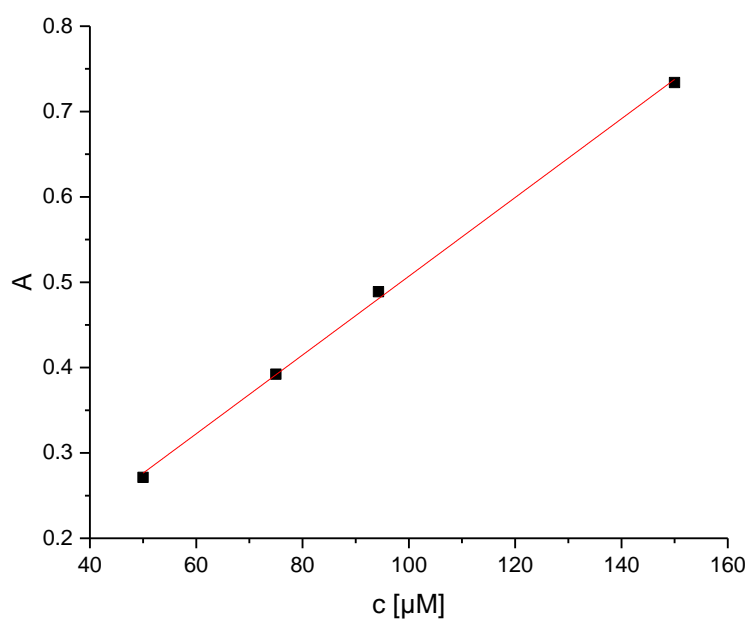


Figure S11: Concentration-dependent UV-vis absorption for determination of extinction coefficient of **5** in CH_2Cl_2 .

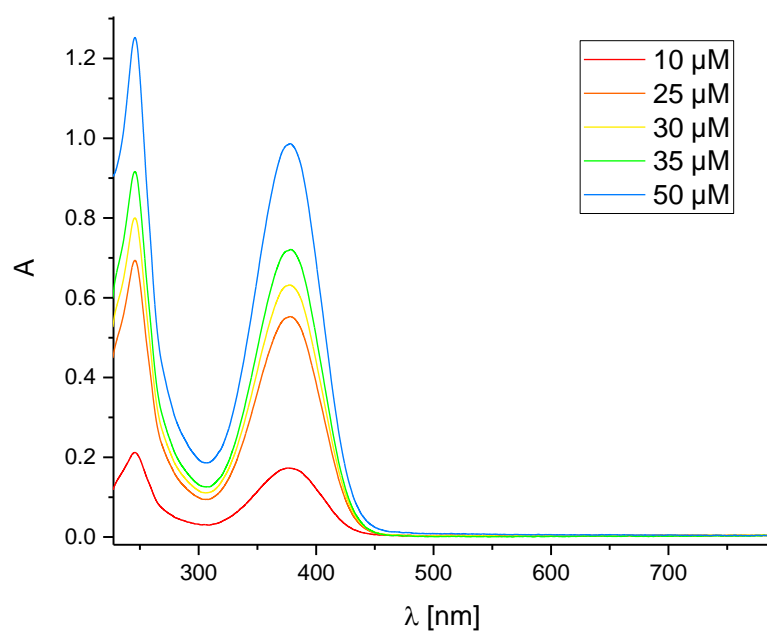


Figure S12: UV–vis absorption spectra of **6** in CH₂Cl₂.

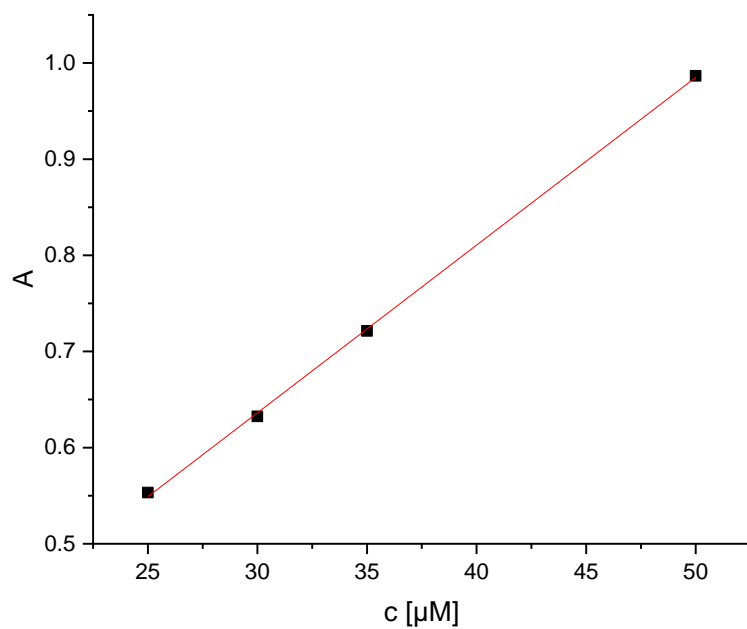


Figure S13: Concentration-dependent UV–vis absorption for determination of extinction coefficient of **6** in CH₂Cl₂.

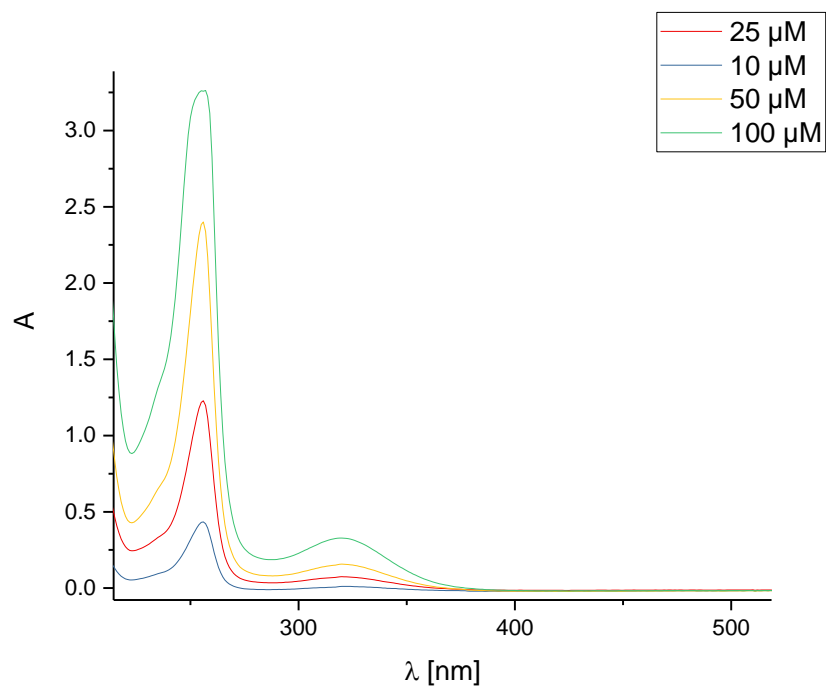


Figure S14: UV–vis absorption spectra of **7** in MeCN.

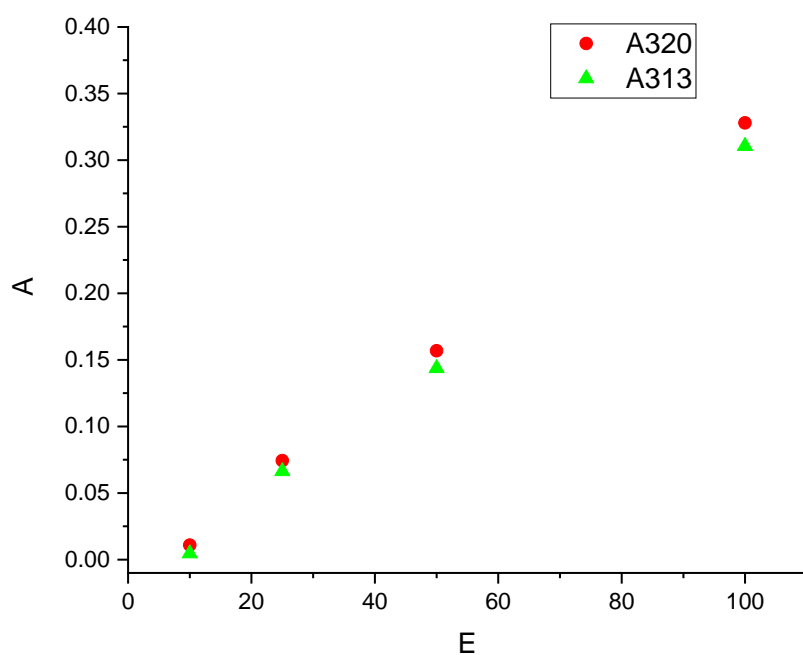


Figure S15: Concentration-dependent UV–vis absorption for determination of extinction coefficient of **7** in MeCN.

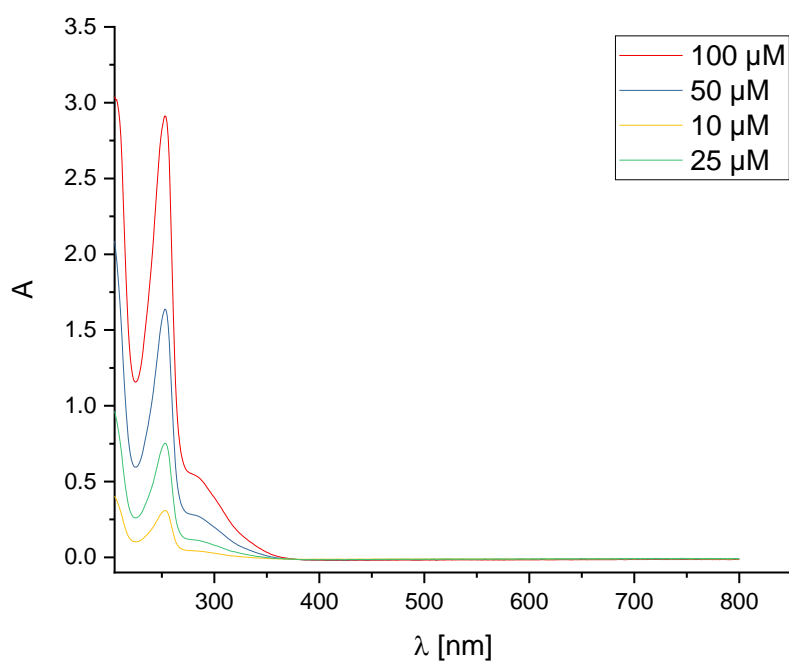


Figure S16: UV-vis absorption spectra of **8** in MeCN.

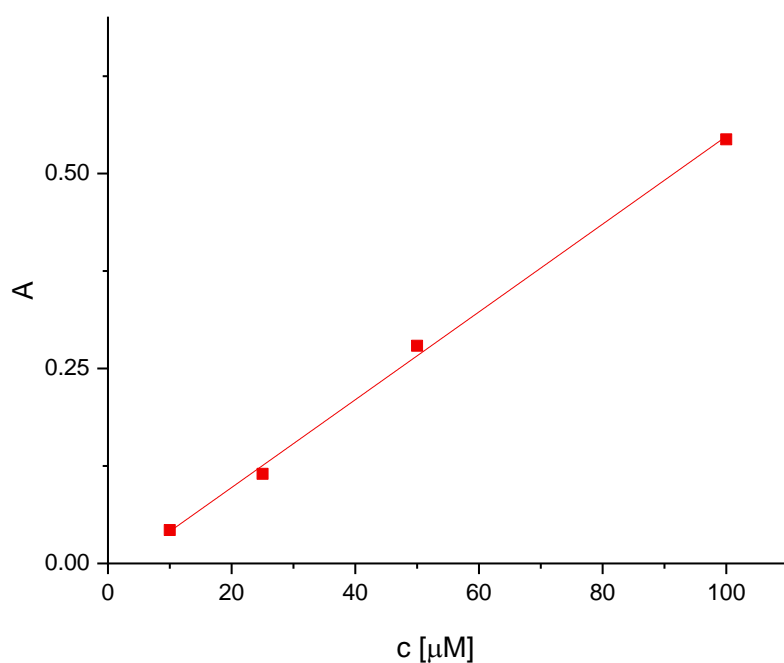


Figure S17: Concentration-dependent UV-vis absorption for determination of extinction coefficient of **8** in MeCN.

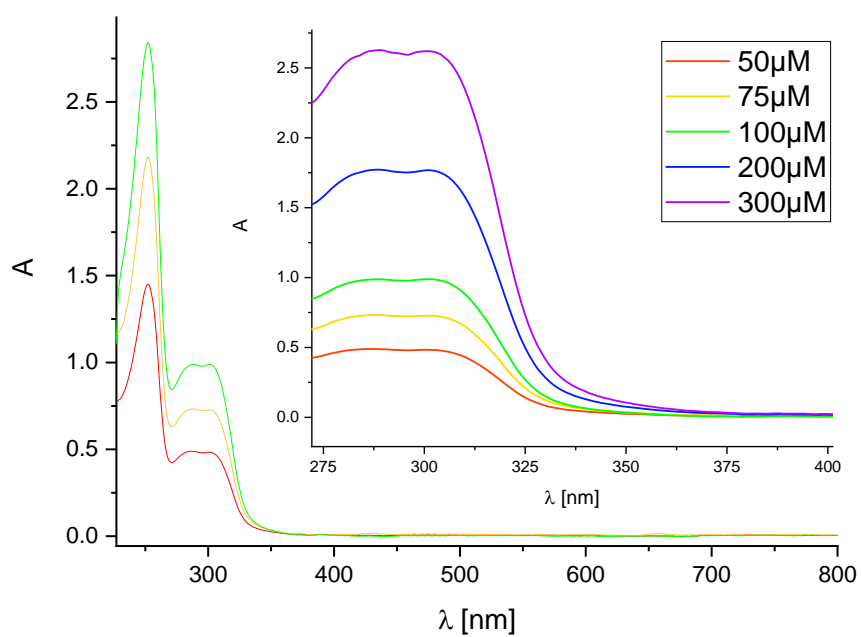


Figure S18: UV–vis absorption spectra of **9** in CH_2Cl_2 .

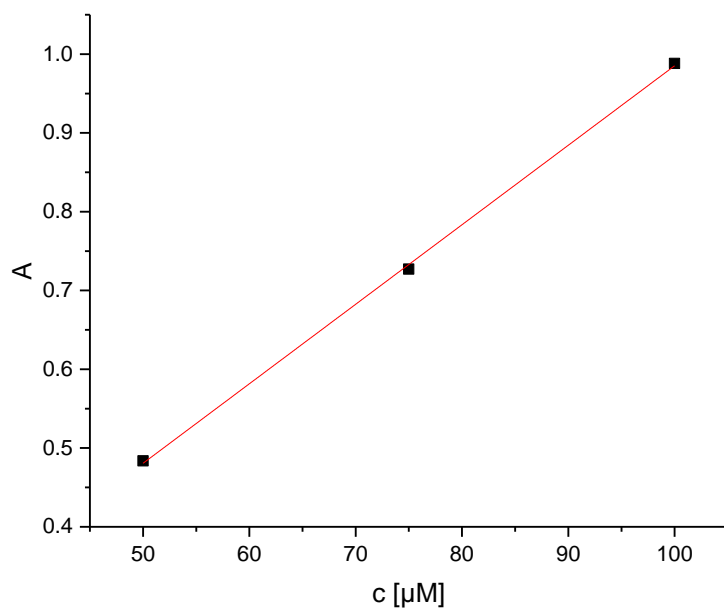


Figure S19: Concentration-dependent UV–vis' absorption for determination of extinction coefficient of **9** in CH_2Cl_2 .

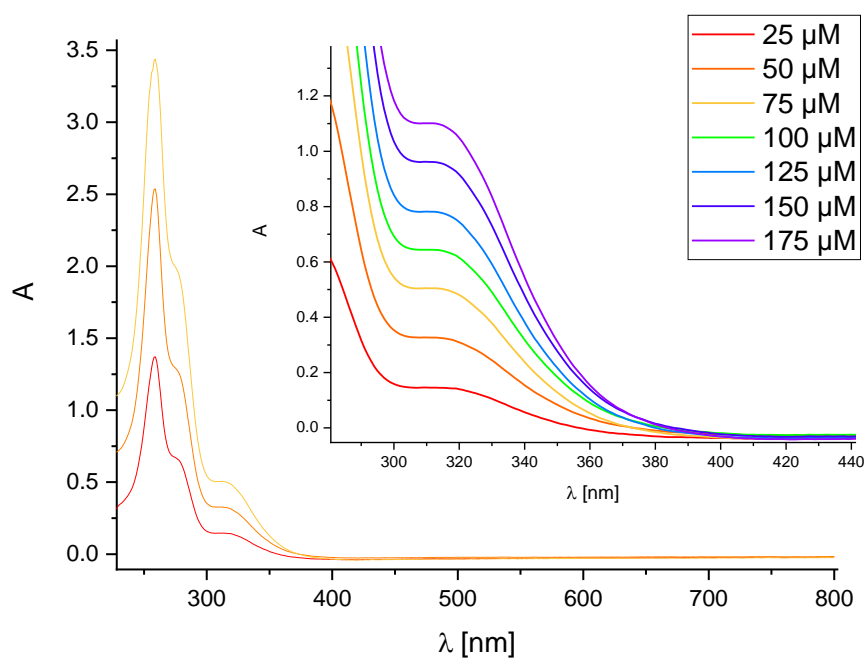


Figure S20: UV-vis absorption spectra of CH_2Cl_2 **10** in CH_2Cl_2 .

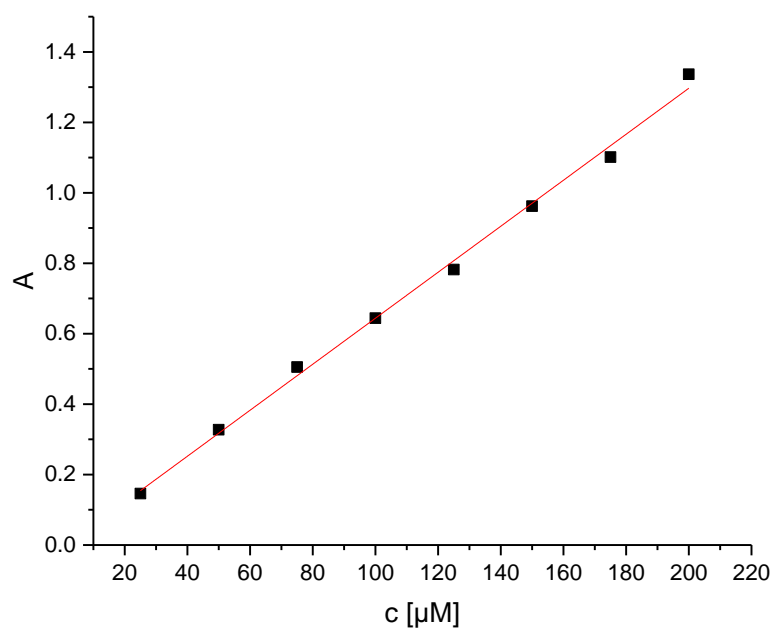


Figure S21: Concentration-dependent UV-vis absorption for determination of extinction coefficient of **10** in CH_2Cl_2 .

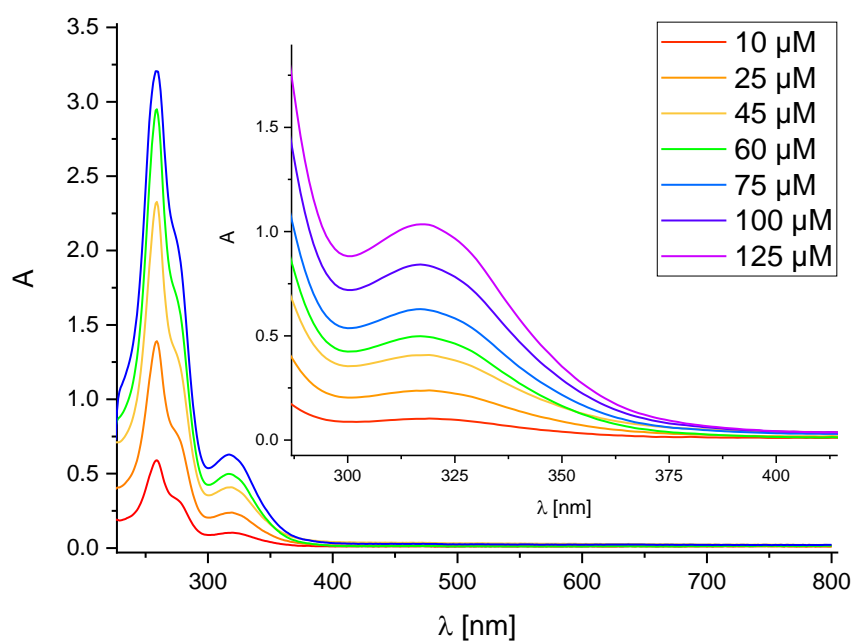


Figure S22: UV–vis absorption spectra of **11** in CH_2Cl_2 .

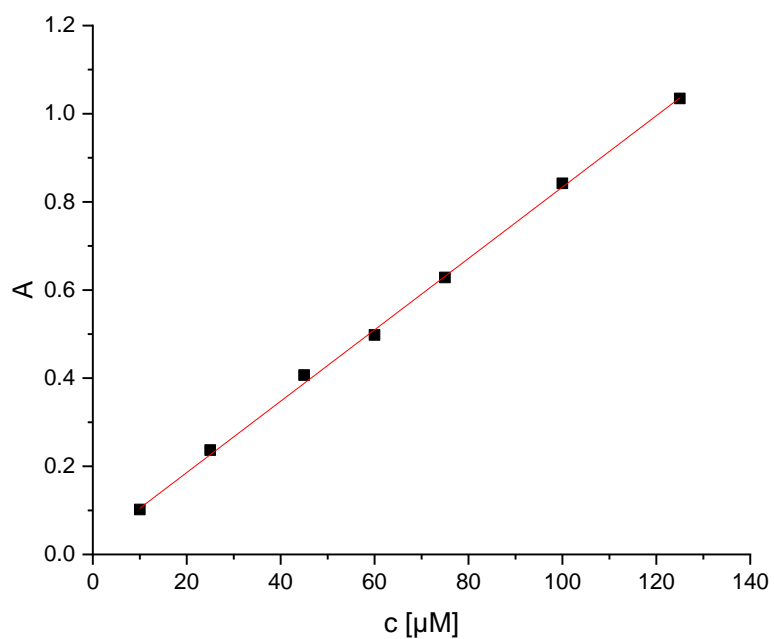


Figure S23: Concentration-dependent UV–vis absorption for determination of extinction coefficient of **11** in CH_2Cl_2 .

Emission

The emission spectra were recorded at 20 °C in acetonitrile (HPLC grade, Fisher Scientific) or dichloromethane (HPLC grade, Fisher Scientific).

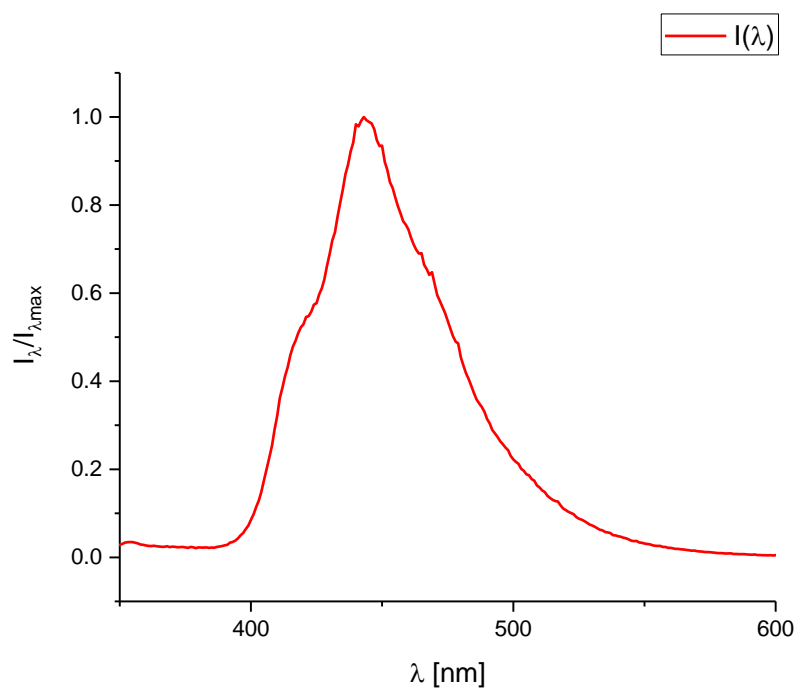


Figure S24: Normalized emission of **1** in MeCN, 100 μ M, λ_{ex} = 320 nm, $\text{slit}_{\text{ex,em}}$ = 5 nm/5 nm.

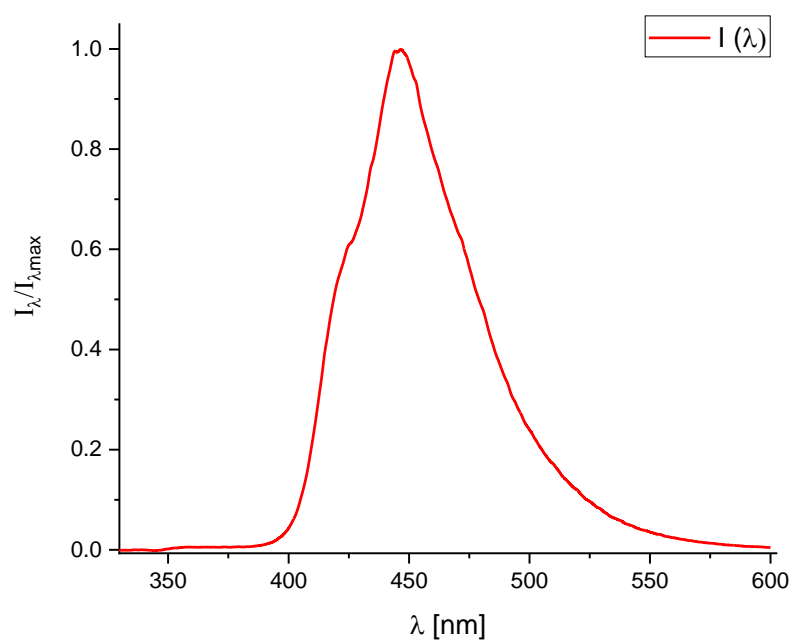


Figure S25: Normalized emission of **2** in CH_2Cl_2 , 100 μM , $\lambda_{\text{ex}} = 313$ nm, slits = 5 nm/5 nm.

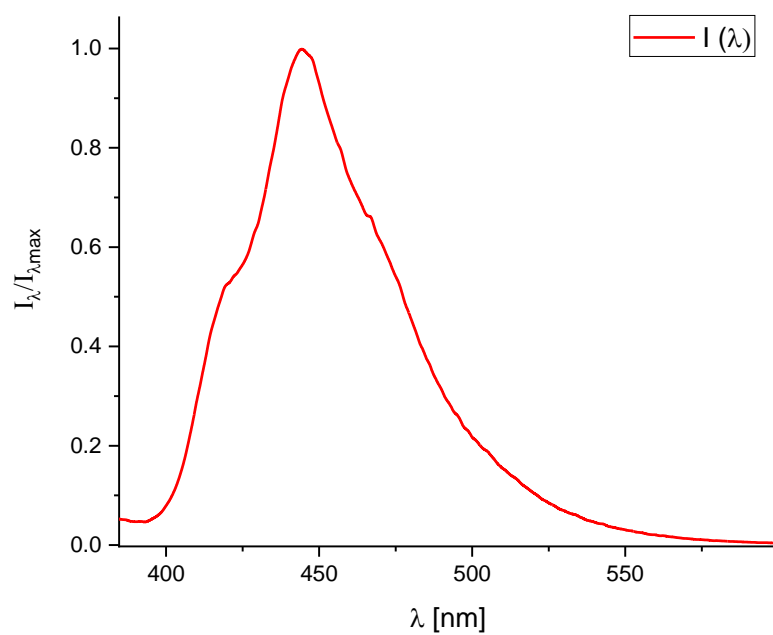


Figure S26: Normalized emission of **3** in CH_2Cl_2 , 100 μM , $\lambda_{\text{ex}} = 320$ nm, slits = 5 nm/5 nm.

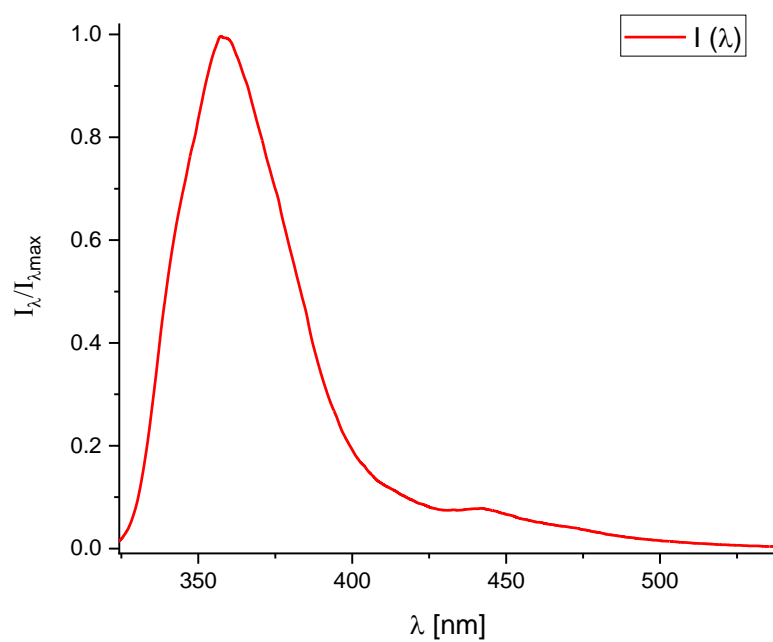


Figure S27: Normalized emission of **4** in MeCN, 100 μ M, λ_{ex} = 310 nm, slits = 3 nm/3 nm.

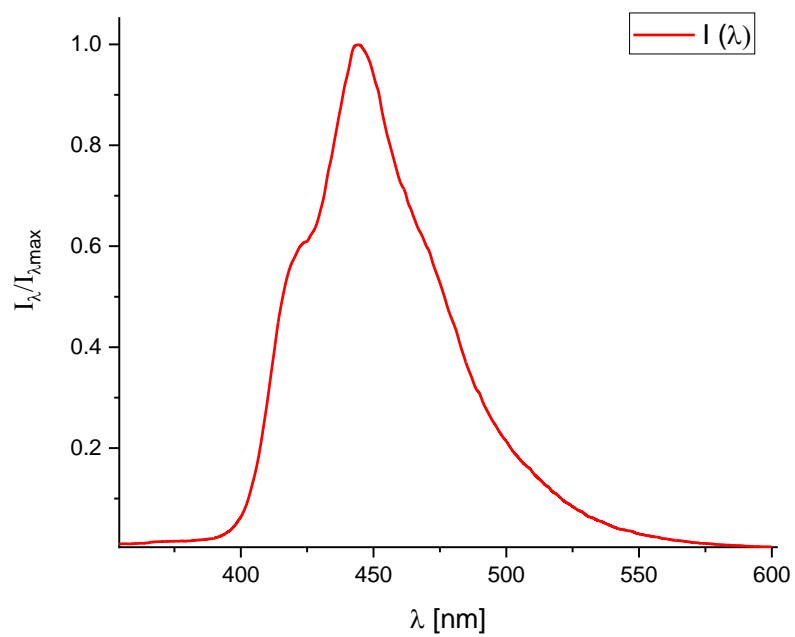


Figure S28: Normalized emission of **5** in CH_2Cl_2 , 100 μM , $\lambda_{\text{ex}} = 328$ nm, slits = 5 nm/5 nm.

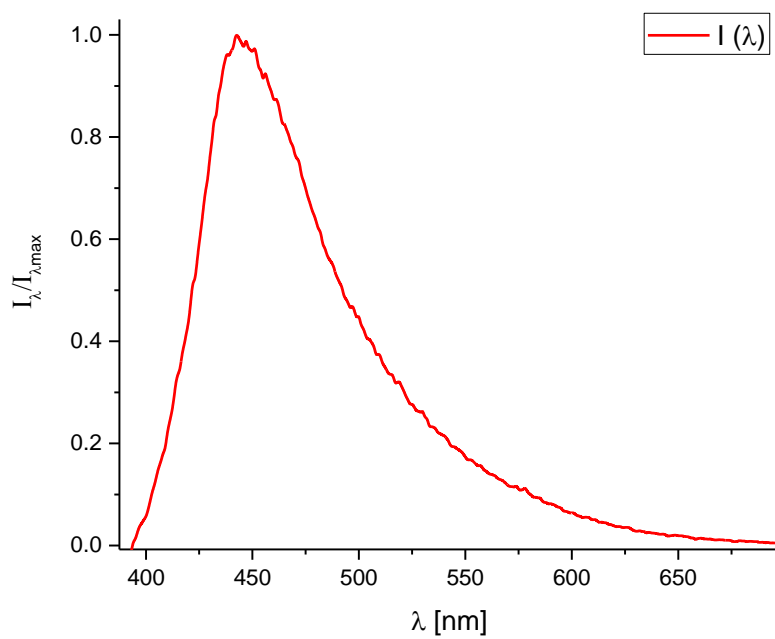


Figure S29: Normalized emission of **6** in MeCN, 50 μM , $\lambda_{\text{ex}} = 378$ nm, slits = 8 nm/8 nm.

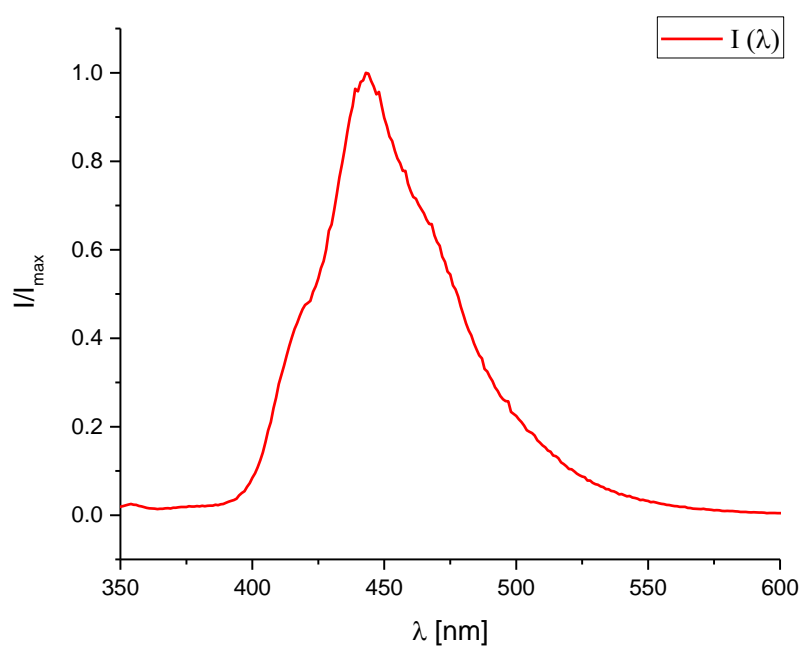


Figure S30: Normalized emission of **7** in MeCN, 100 μ M, λ_{ex} = 320 nm, slit_{ex/em} = 5 nm/5 nm.

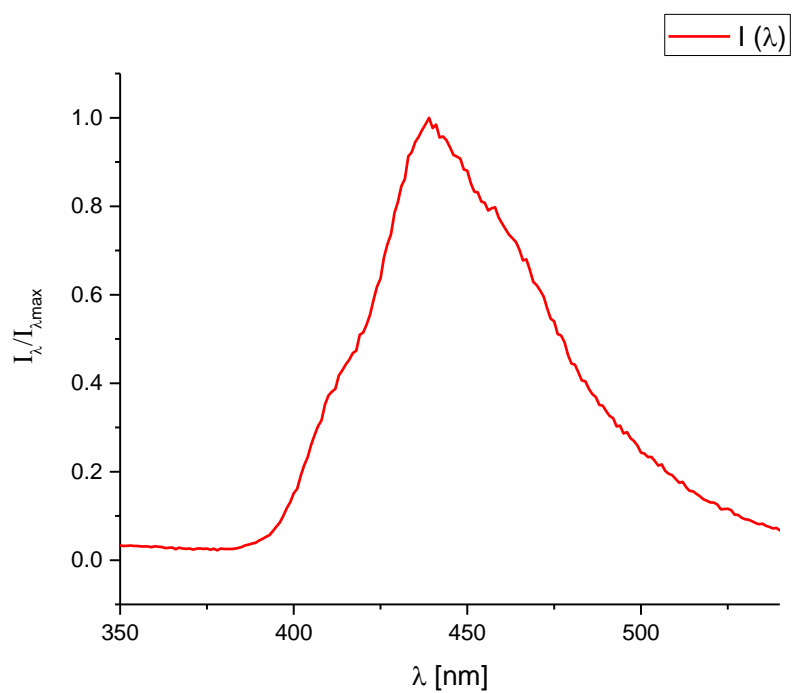


Figure S31: Normalized emission of **8** in MeCN; 100 μM , $\lambda_{\text{ex}} = 280 \text{ nm}$, $\text{slit}_{\text{ex/em}} = 5 \text{ nm}/5 \text{ nm}$.

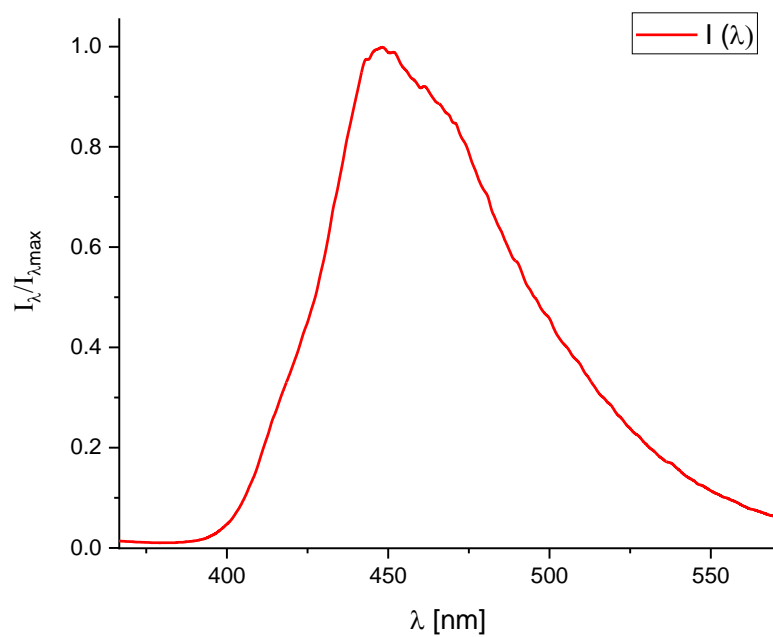


Figure S32: Normalized emission of **9** in CH_2Cl_2 , 100 μM , $\lambda_{\text{ex}} = 300$ nm, slits = 5 nm/5 nm.

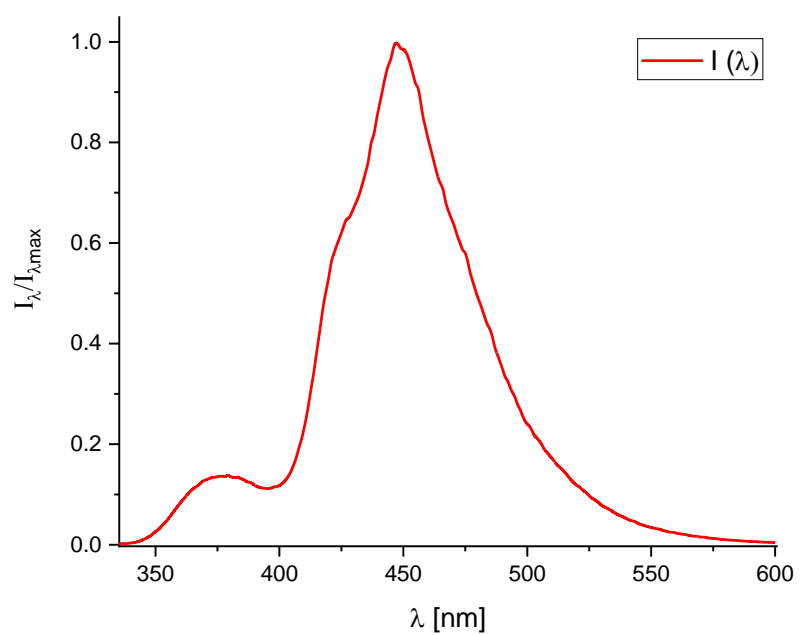


Figure S33: Normalized emission of **10** in CH_2Cl_2 , 100 μM , $\lambda_{\text{ex}} = 310$ nm, slits = 5 nm/5 nm.

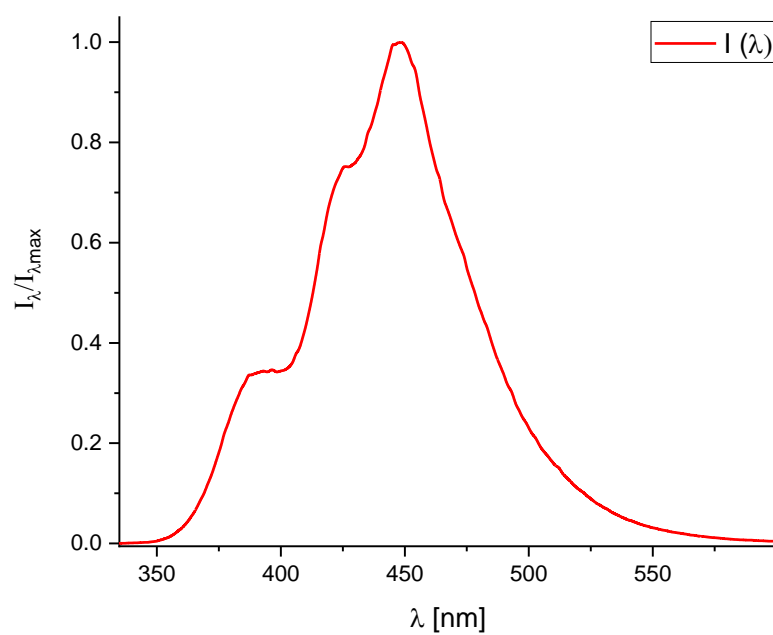


Figure S34: Normalized emission of **11** in CH_2Cl_2 , 100 μM , $\lambda_{\text{ex}} = 317$ nm, slits = 6 nm/6 nm.

Cyclic voltammetry data

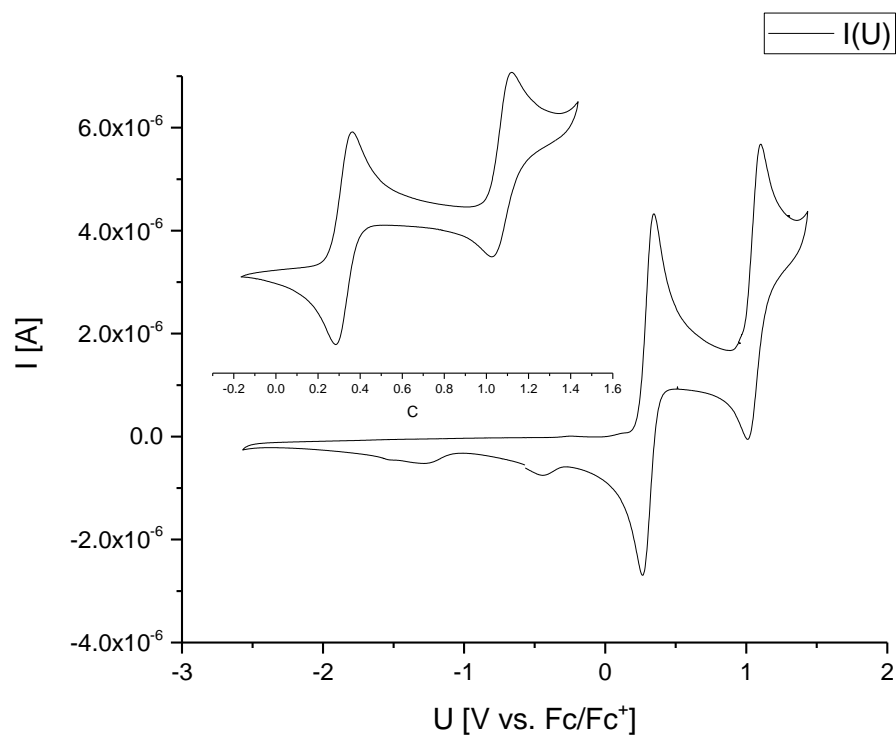


Figure S35: Cyclovoltammetry of **1** in MeCN (0.05 M NBu₄PF₆), $V_s = 100 \text{ mVs}^{-1}$, referenced vs. Fc/Fc⁺.

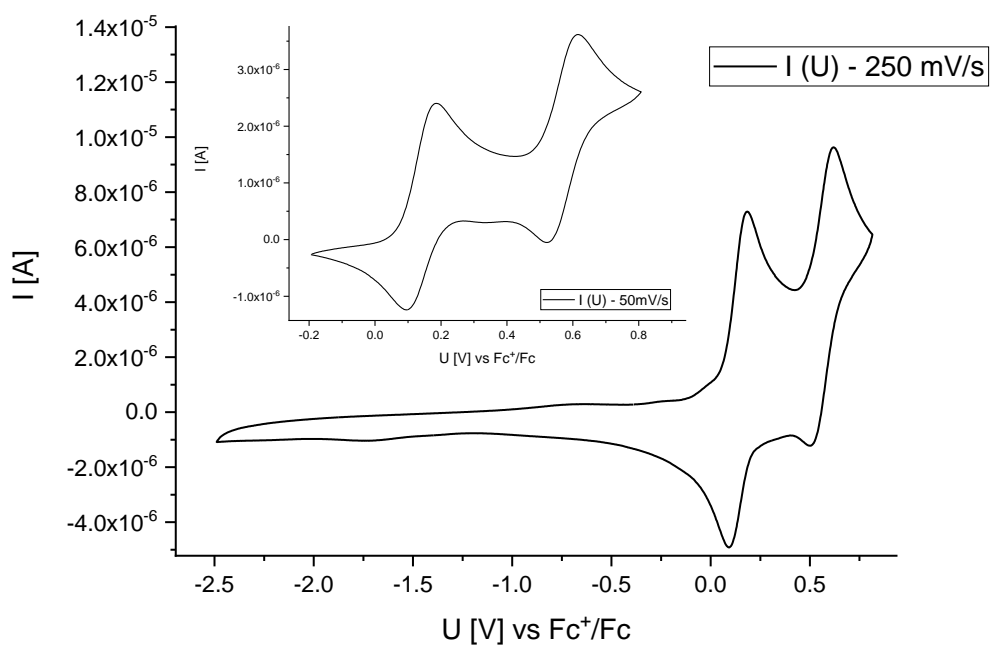


Figure S36: Cyclic voltammetry of **2** in CH_2Cl_2 (0.05 M NBu_4PF_6), $V_s = 50\text{mV/s}$ and 250 mV/s , referenced vs. Fc/Fc^+ .

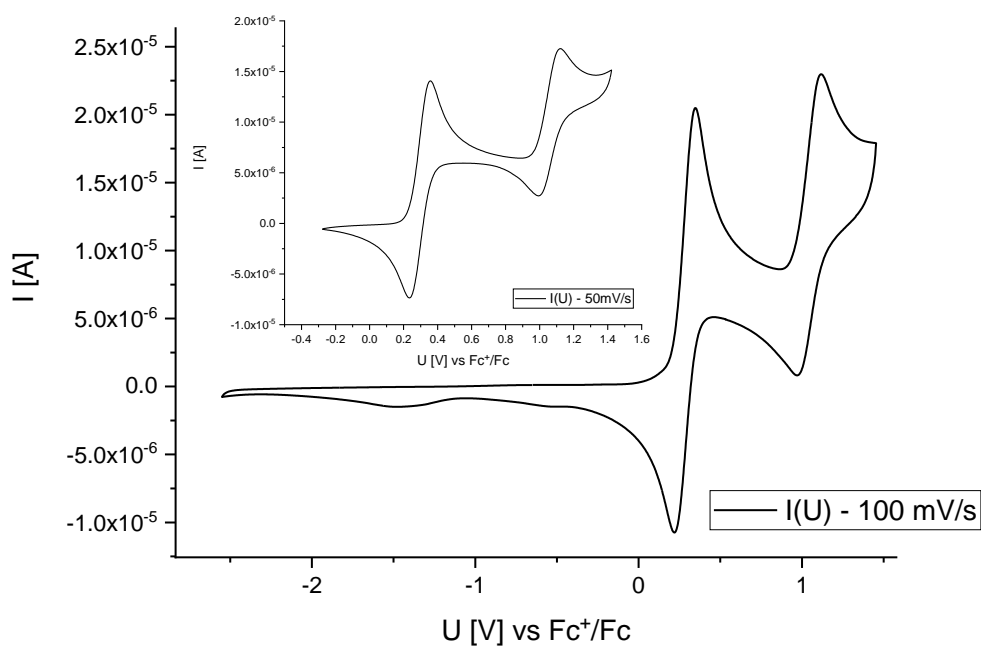


Figure S37: Cyclic voltammetry of **3** in MeCN (0.05 M NBu₄PF₆), $V_s = 50$ mV/s and 100 mV/s, referenced vs. Fc/Fc⁺.

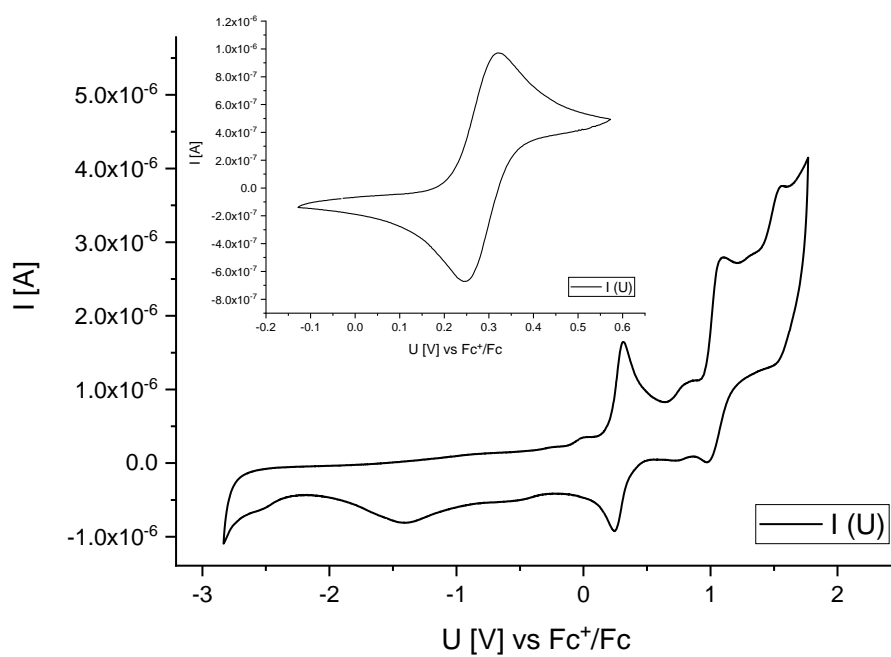


Figure S38: Cyclic voltammetry of **4** in MeCN (0.05 M NBu₄PF₆), $V_s = 250$ mV/s, referenced vs. Fc/Fc⁺.

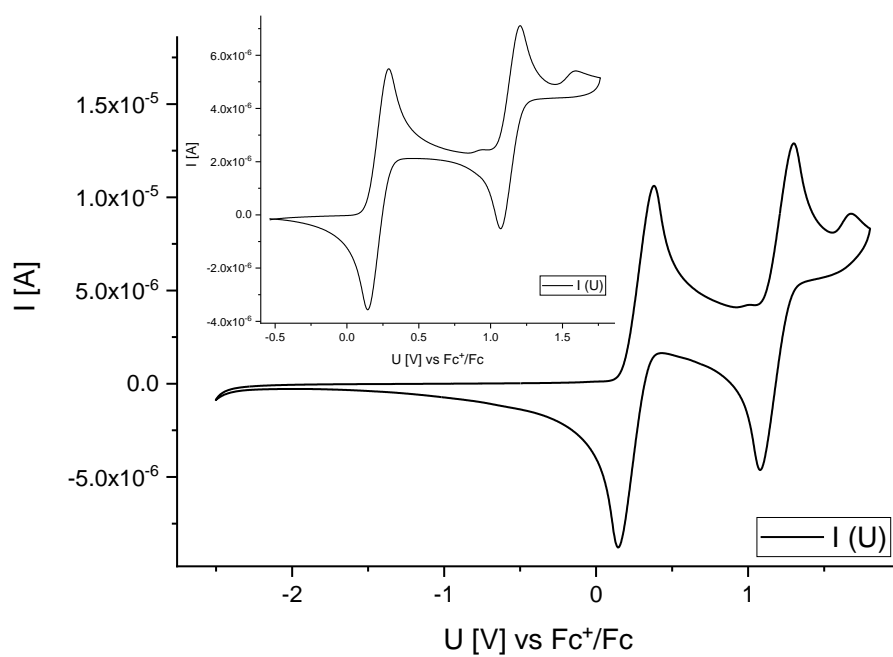


Figure S39: Cyclic voltammetry of **5** in CH_2Cl_2 (0.05 M NBu_4PF_6), $V_s = 250 \text{ mV/s}$, referenced vs. Fc/Fc^+ .

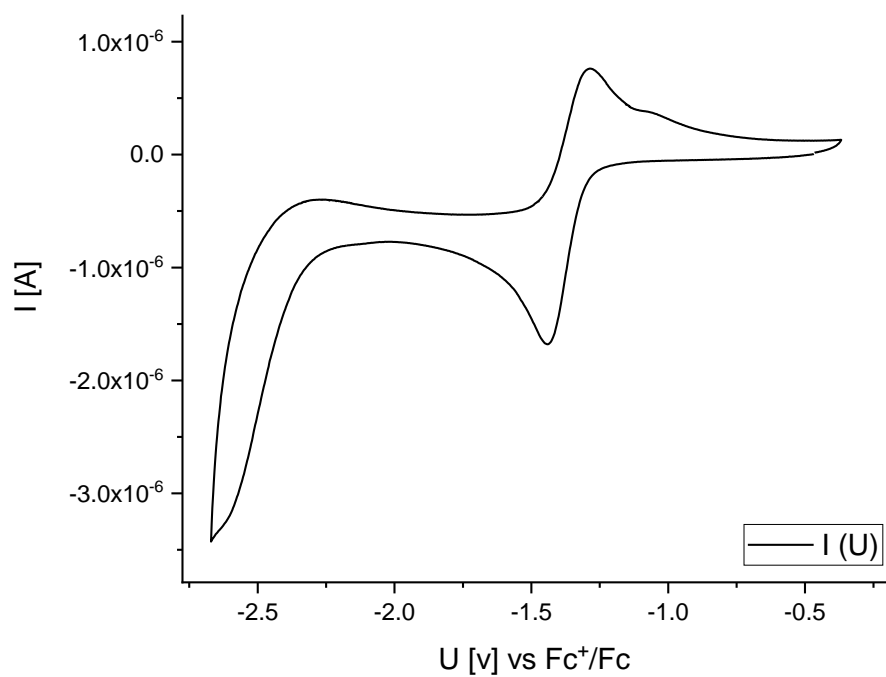
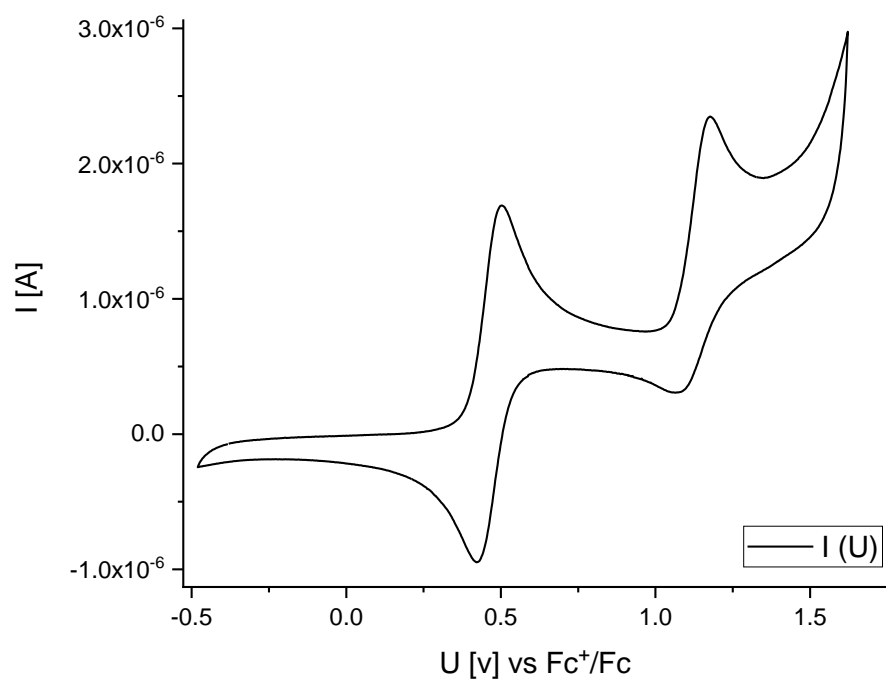


Figure S40: Cyclovoltammetry of **6** in MeCN (0.05 M NBu₄PF₆), $V_s = 100$ mV/s, referenced vs. Fc/Fc⁺.

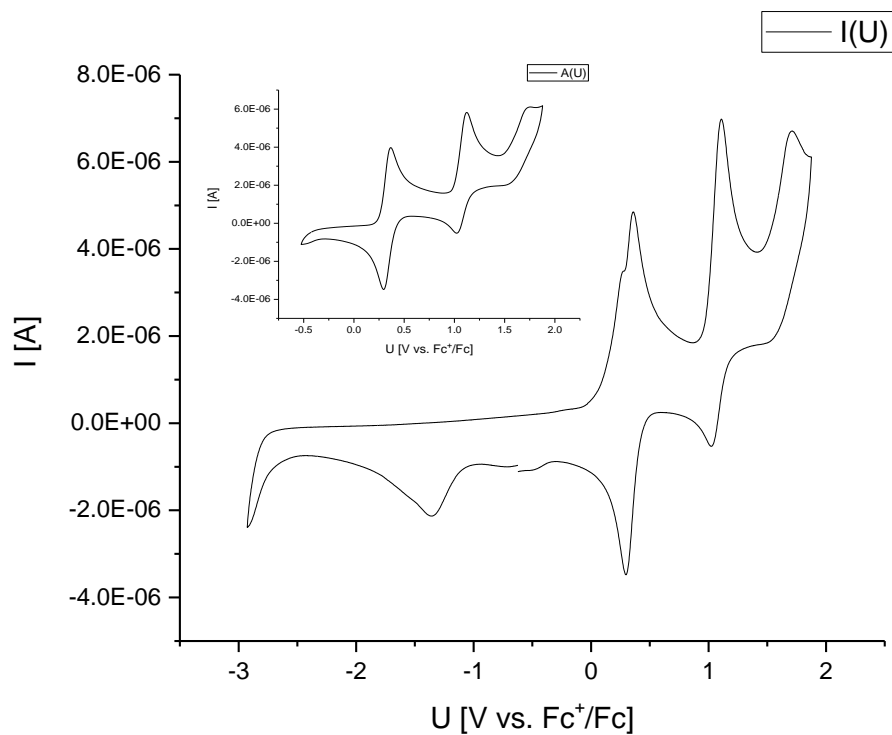


Figure S41: Cyclic voltammetry of **7** in MeCN (0.05 M NBu₄PF₆), $V_s = 250$ mV/s, referenced vs. Fc/Fc⁺. Reduction at -1.3V belongs to irreversible reduction induced by irreversible oxidation second potential.

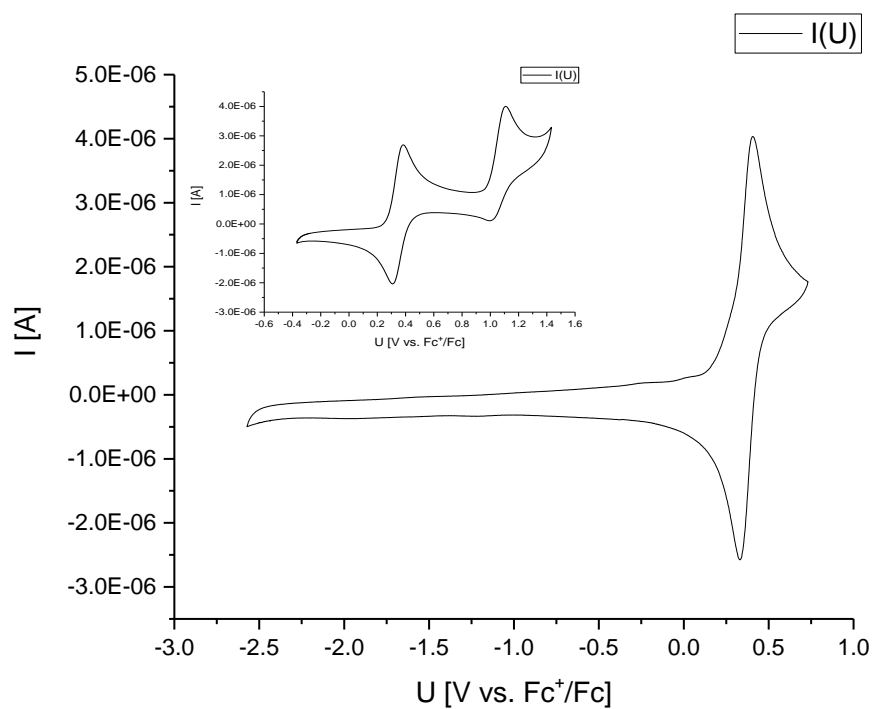


Figure S42: Cyclic voltammetry of **8** in MeCN (0.05 M NBu₄PF₆), $V_s = 250$ mV/s, referenced vs. Fc/Fc⁺. Irreversible reduction bands are coming up if scanning higher than first oxidation.

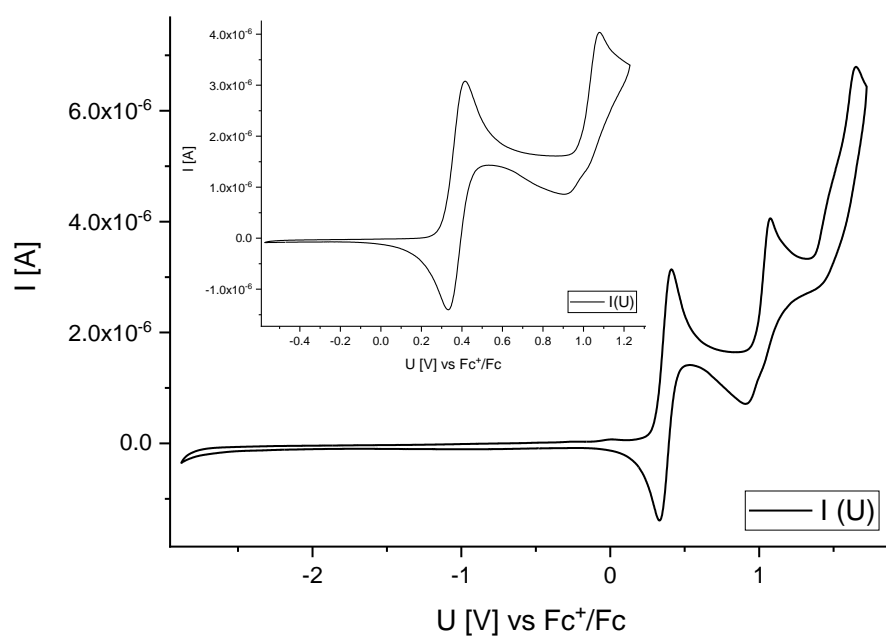


Figure S43: Cyclovoltammetry of **9** in MeCN (0.05 M NBu₄PF₆), $V_s = 50$ mV/s, referenced vs. Fc/Fc⁺.

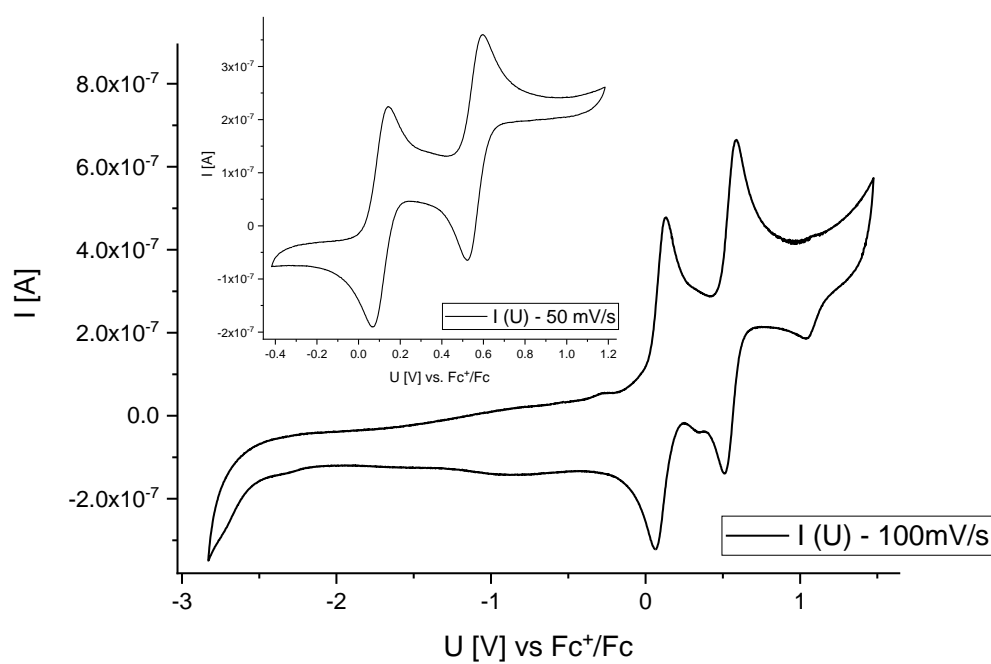


Figure S44: Cyclic voltammetry of **10** in MeCN (0.05 M NBu₄PF₆), *V_s* = 50 mV/s and 100 mV/s., referenced vs. Fc/Fc⁺.

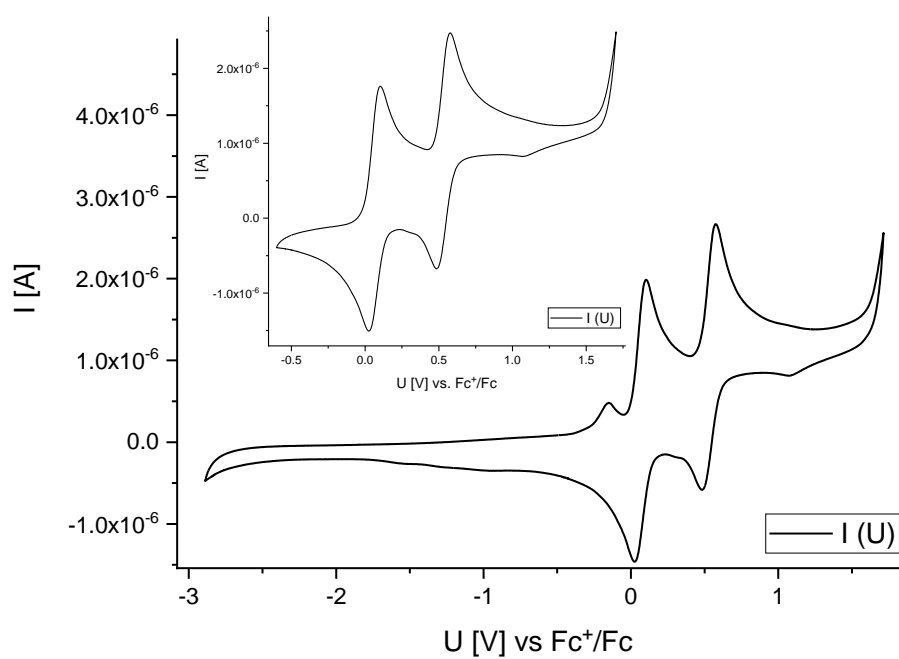


Figure S45: Cyclic voltammetry of **11** in MeCN (0.05 M NBu₄PF₆), $V_s = 100$ mV/s, referenced vs. Fc/Fc⁺.

NMR spectroscopic data

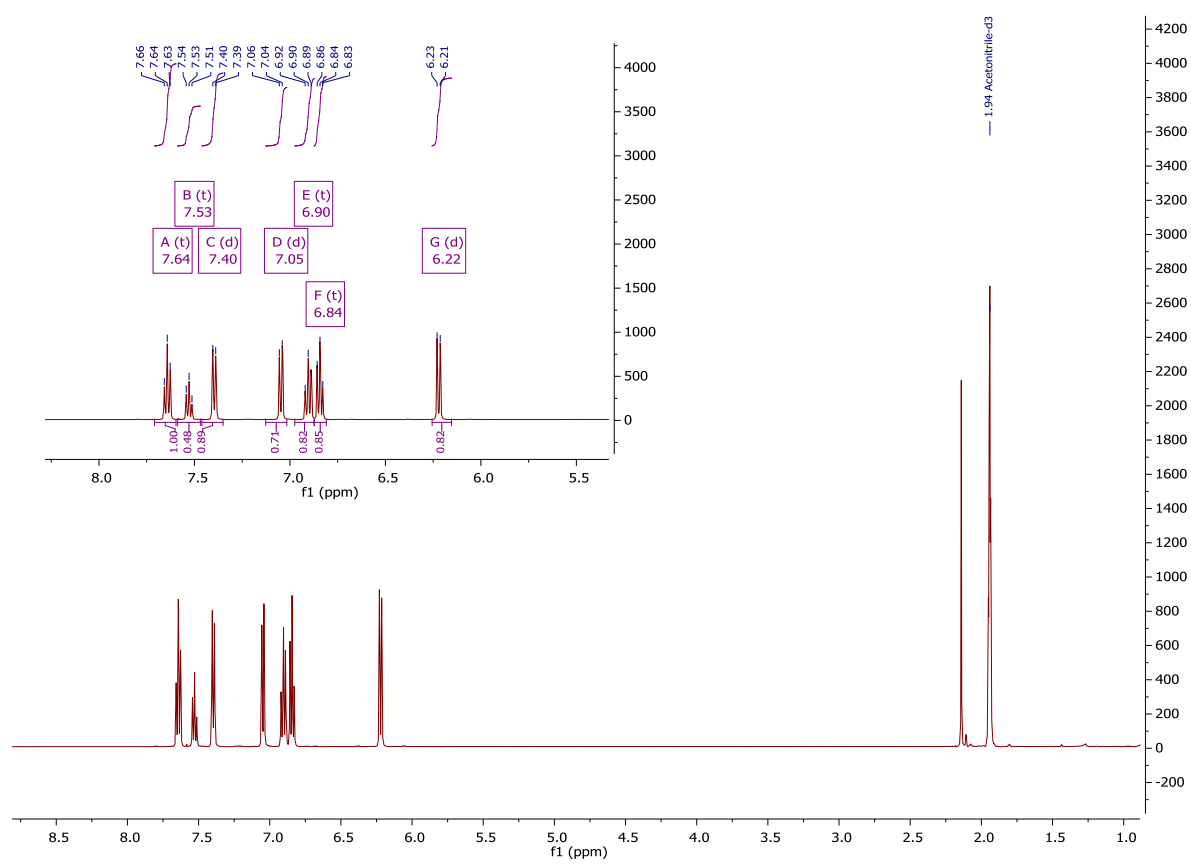


Figure S46: ¹H NMR spectrum of **1**.

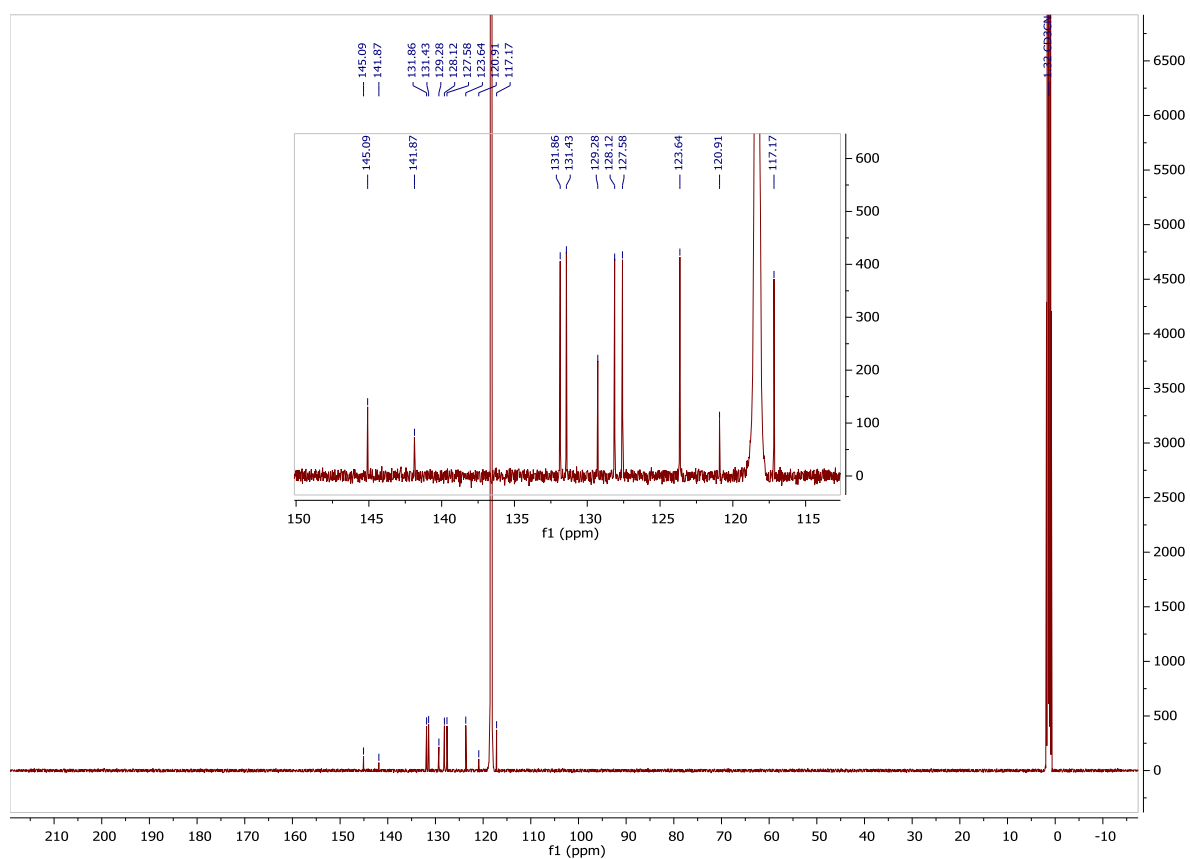


Figure S47: ¹³C NMR spectrum of **1**.

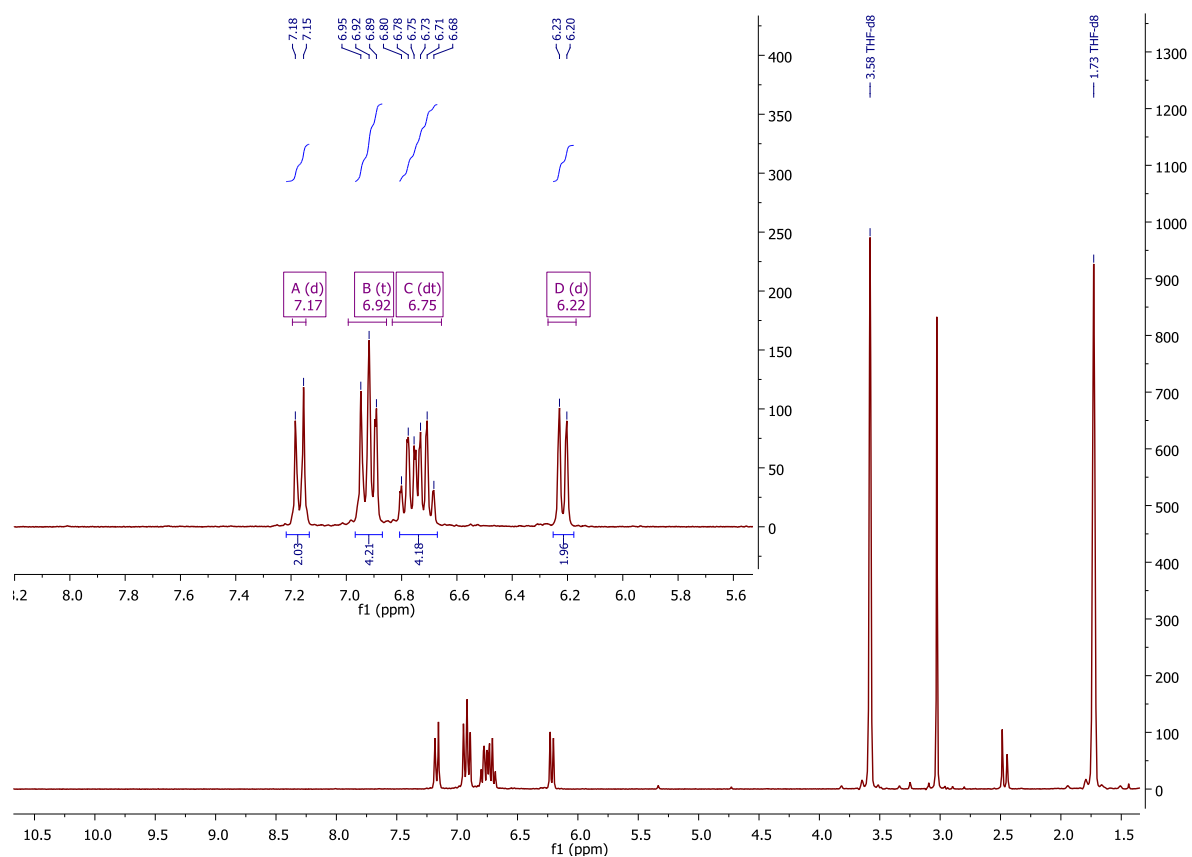


Figure S48: ¹H NMR spectrum of **2**.

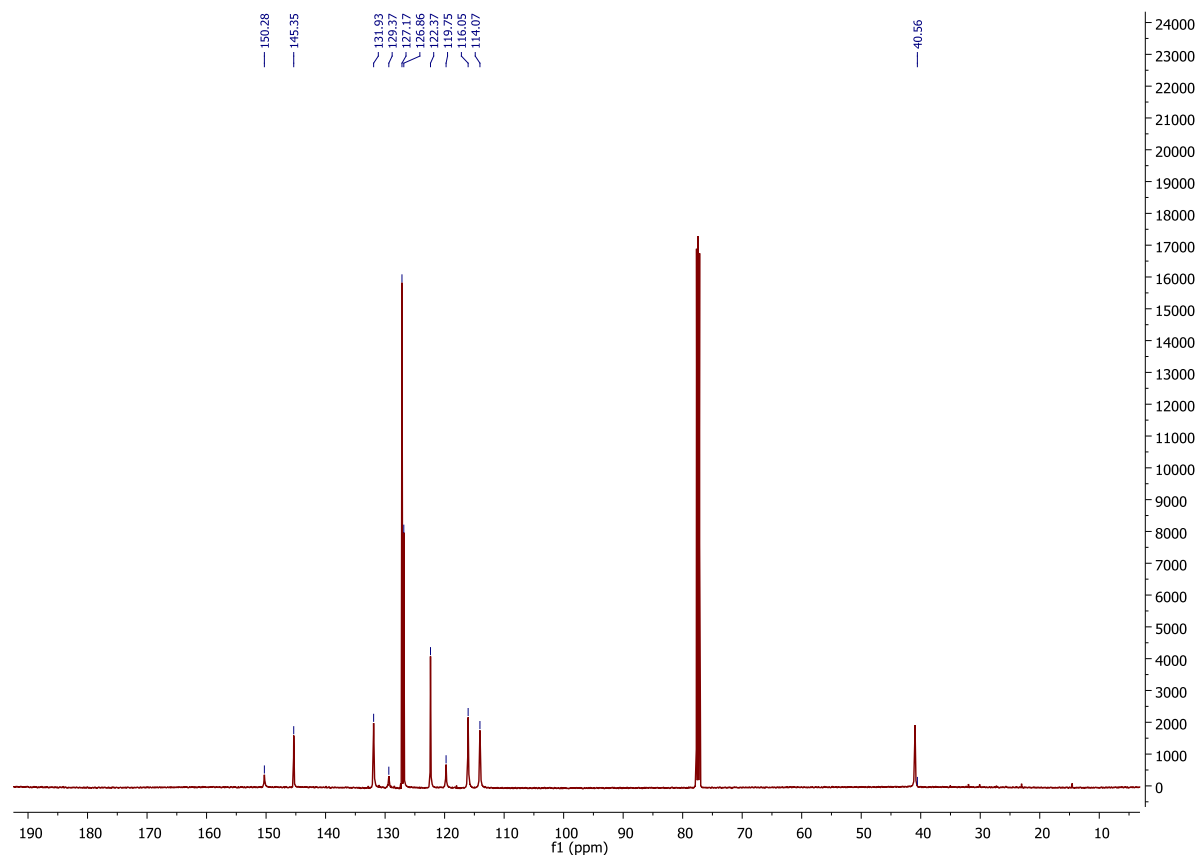


Figure S49: ¹³C NMR spectrum of **2**.

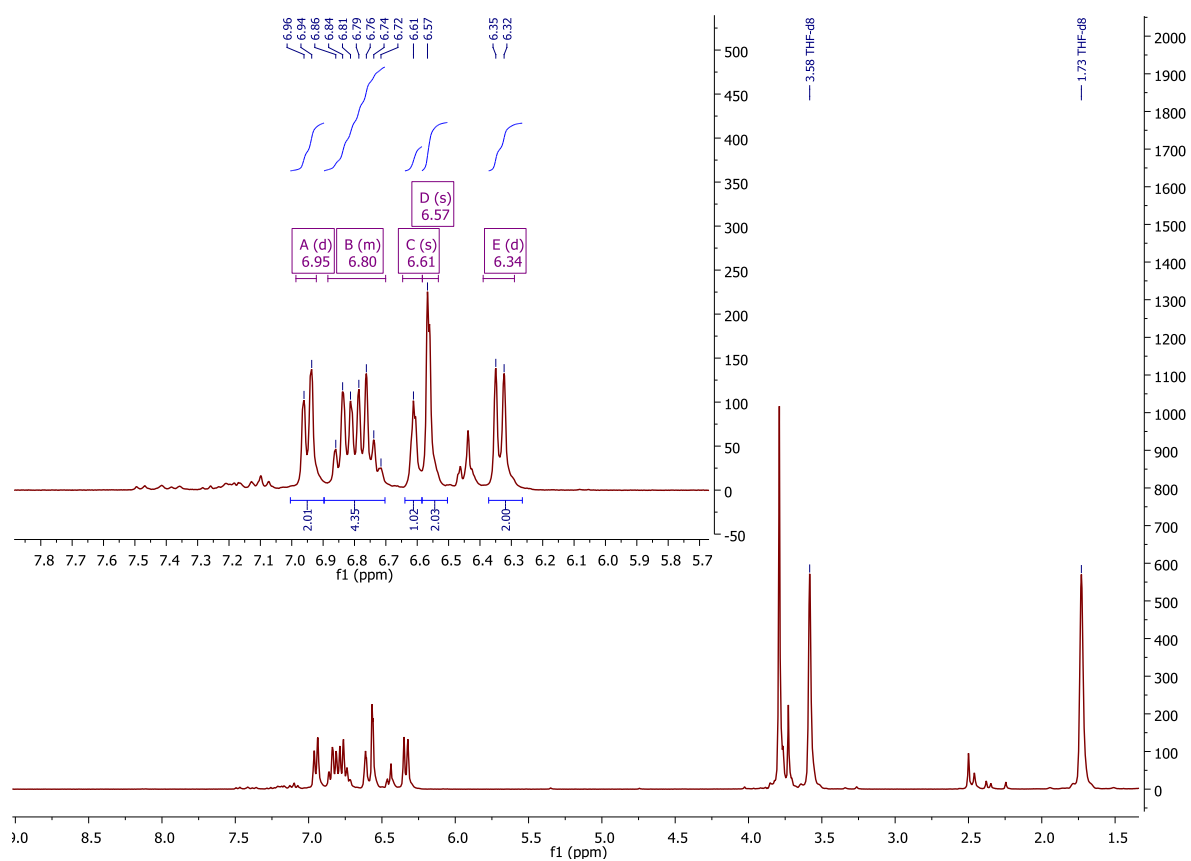


Figure S50: ¹H NMR spectrum of **3**.

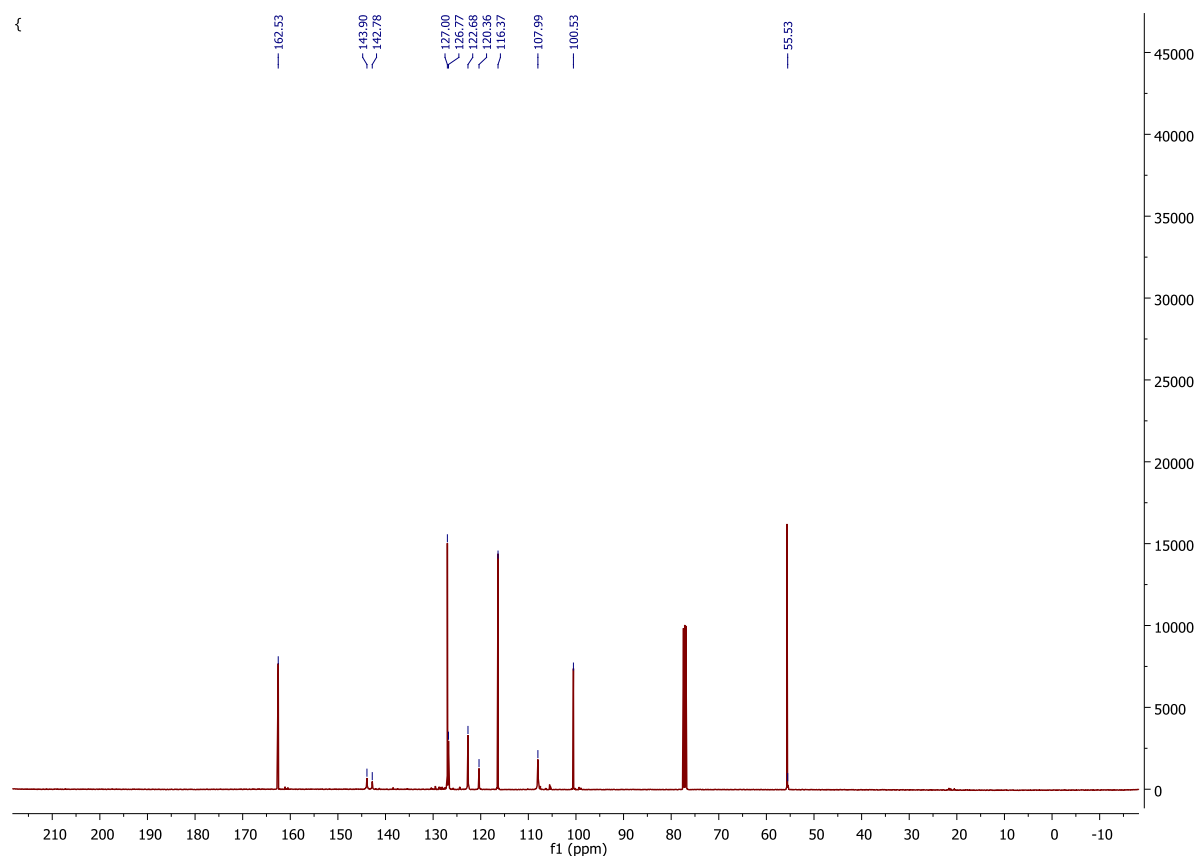


Figure S51: ¹³C NMR spectrum of **3**.

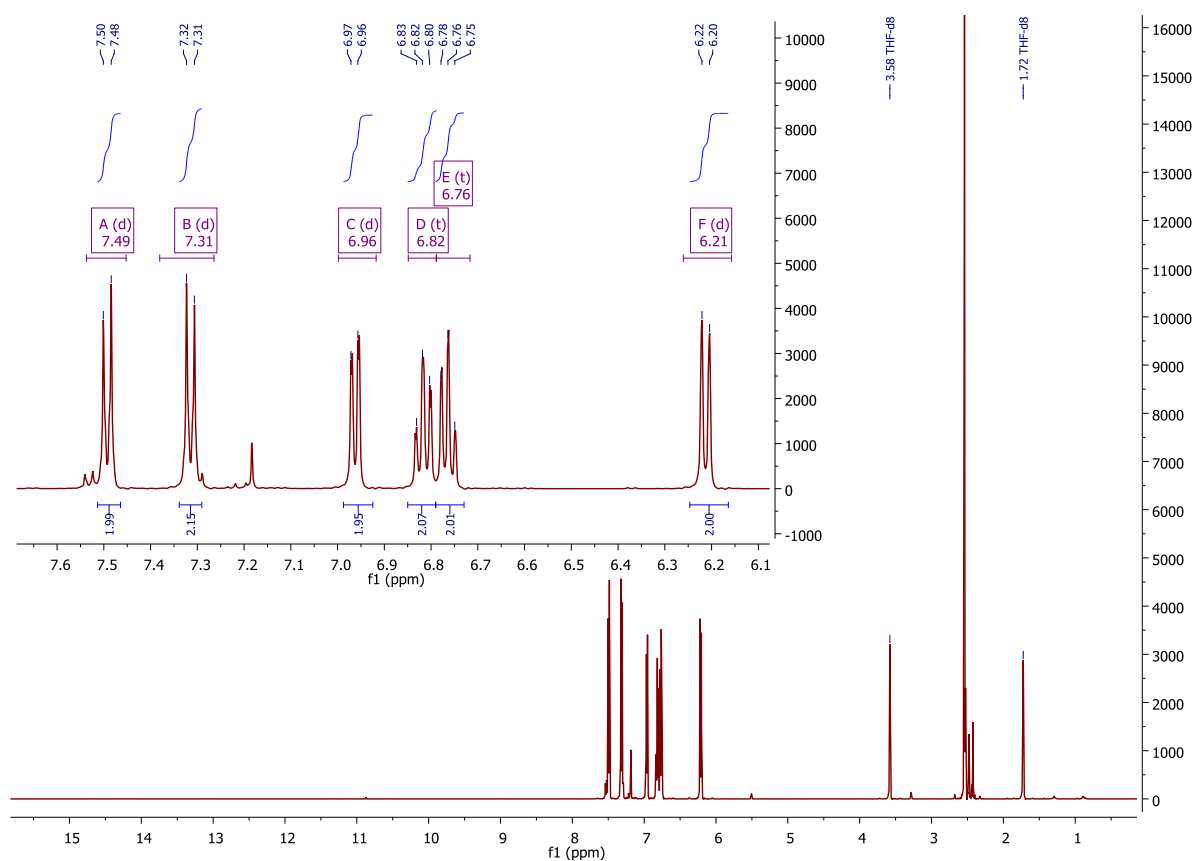


Figure S52: ¹H NMR spectrum of **4**.

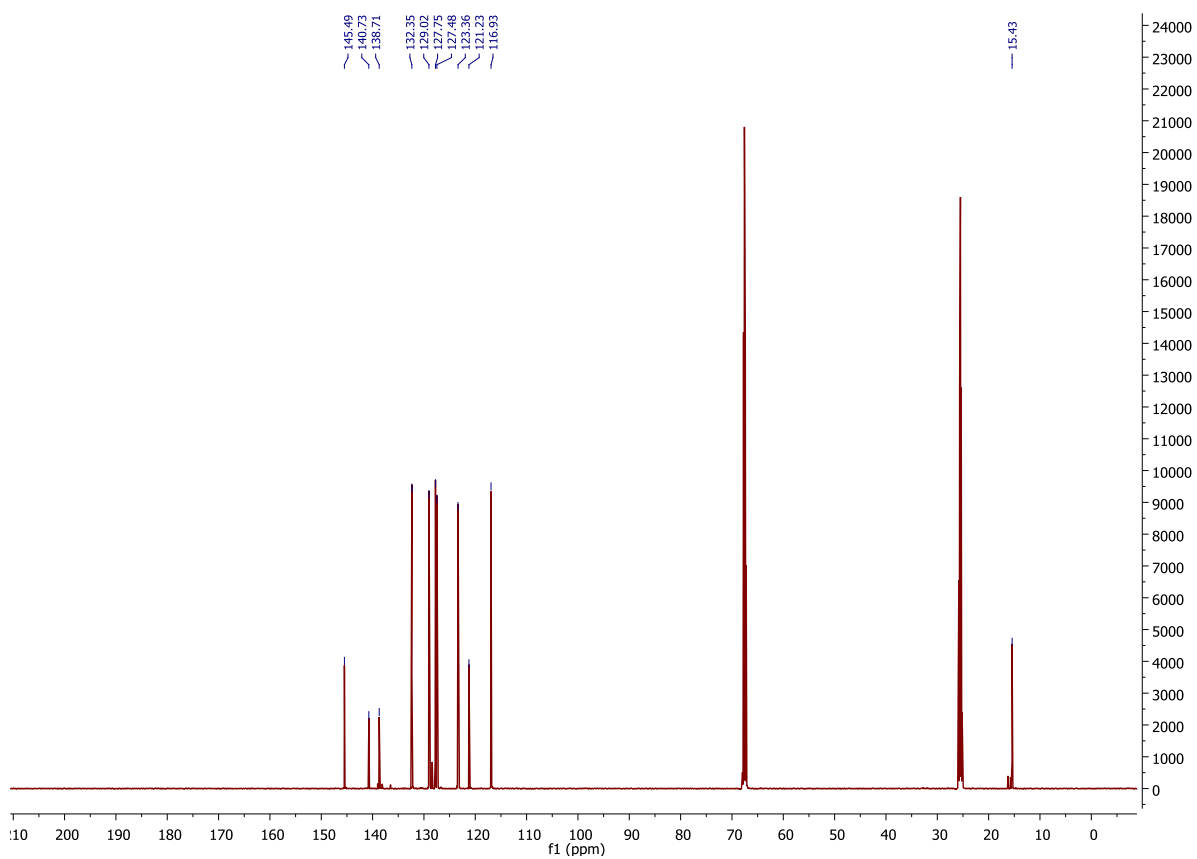


Figure S53: ¹³C NMR spectrum of **4**.

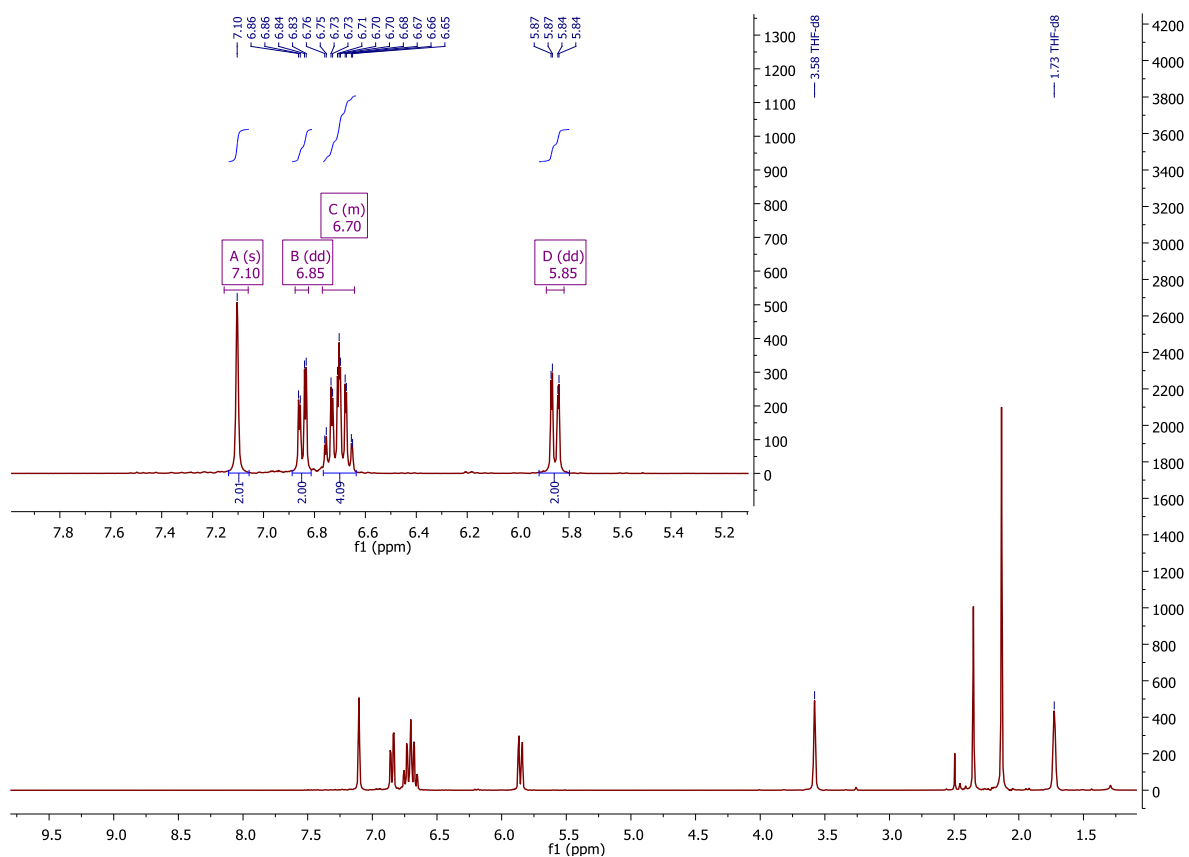


Figure S54: ¹H NMR spectrum of **5**.

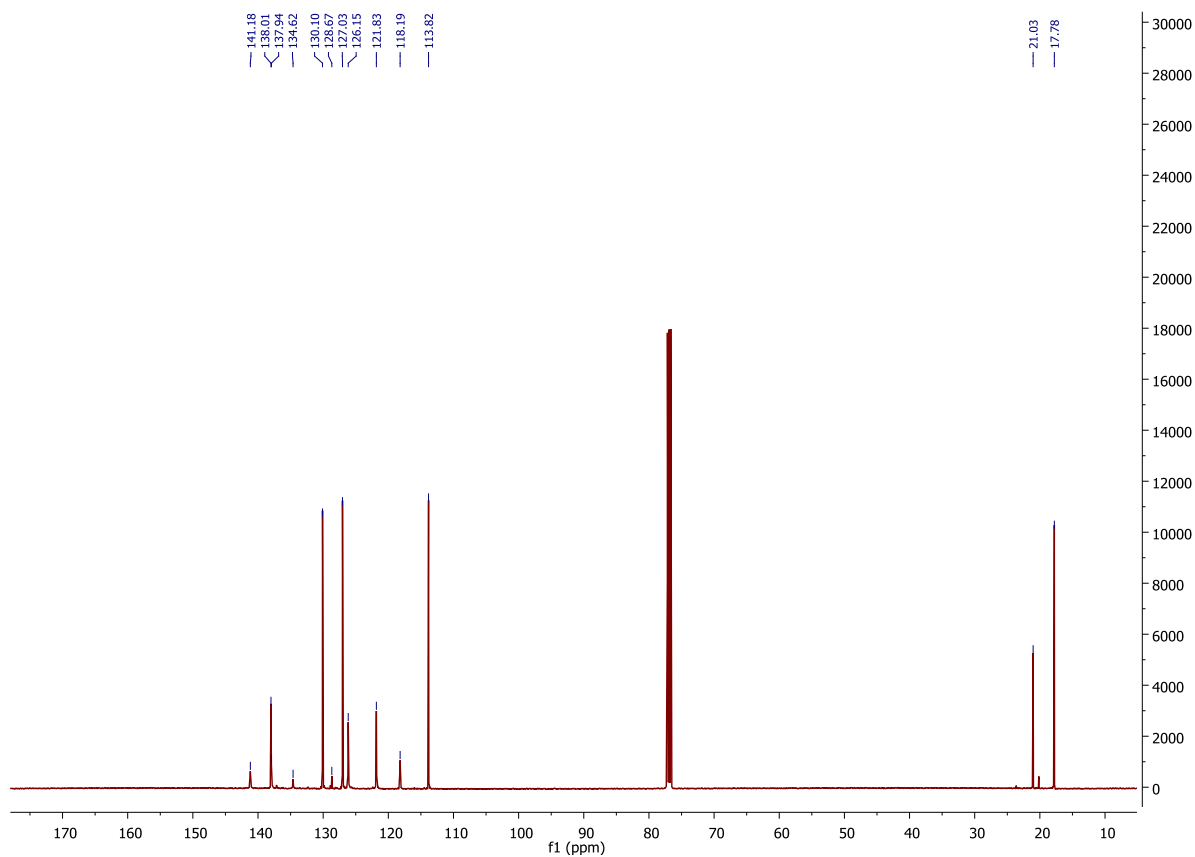


Figure S55: ¹³C NMR spectrum of **5**.

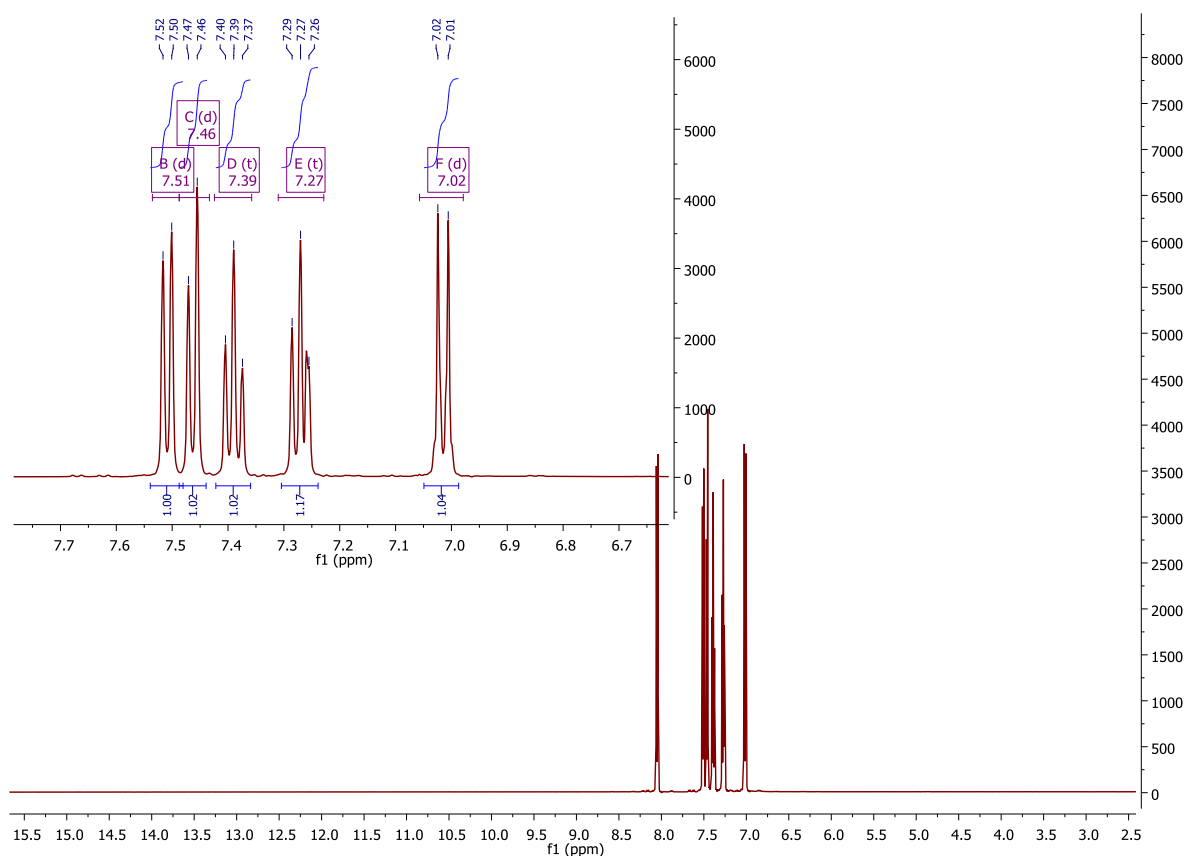


Figure S56: ¹H NMR spectrum of **6**.

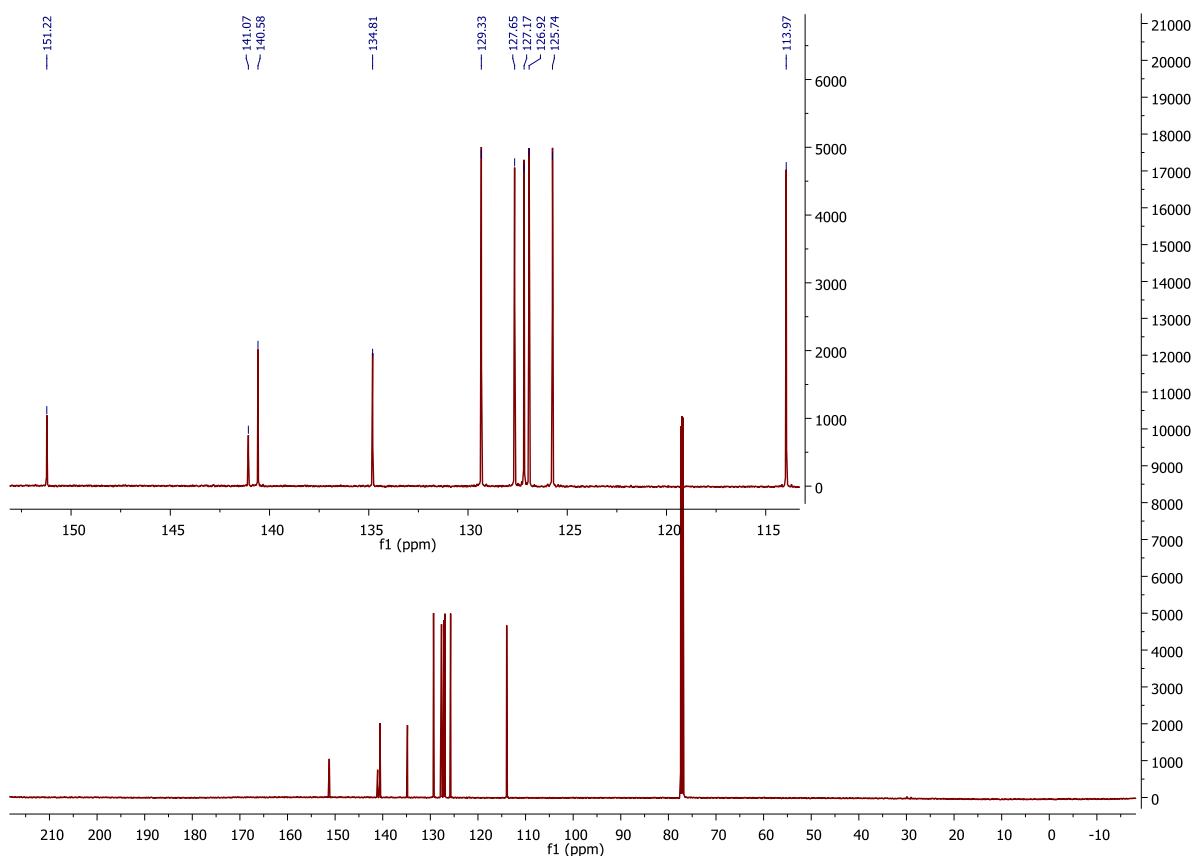


Figure S57: ¹³C NMR spectrum of **6**.

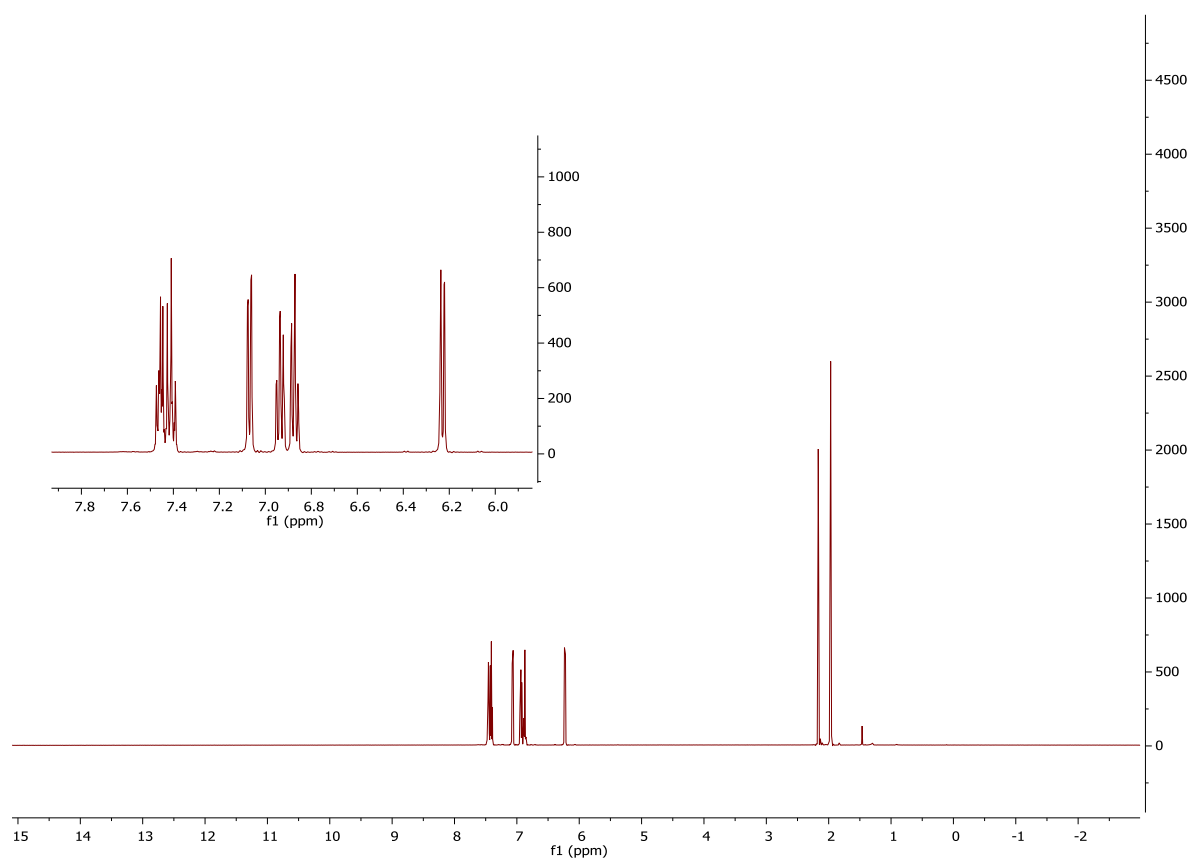


Figure S58: ^1H NMR spectrum of **7**.

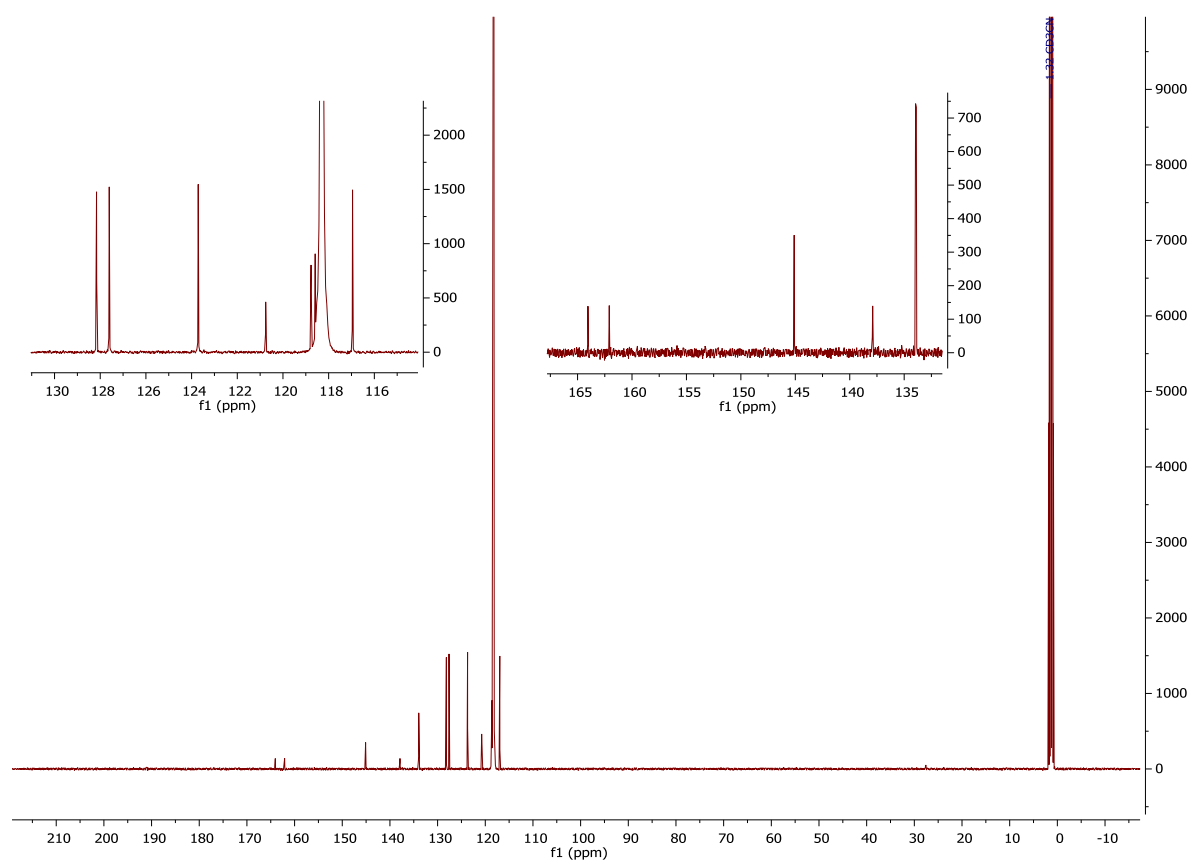


Figure S59: ^{13}C NMR spectrum of **7**.

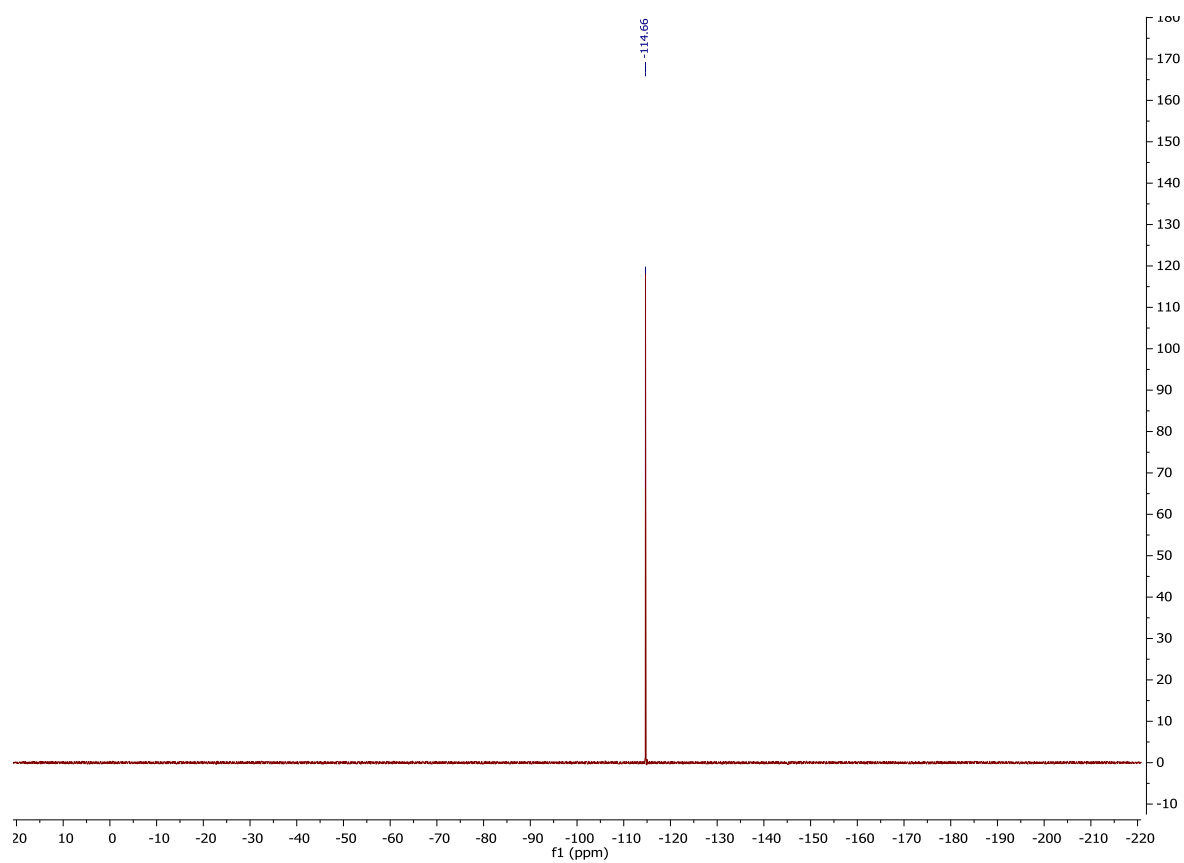


Figure S60: ^{19}F NMR spectrum of **7**.

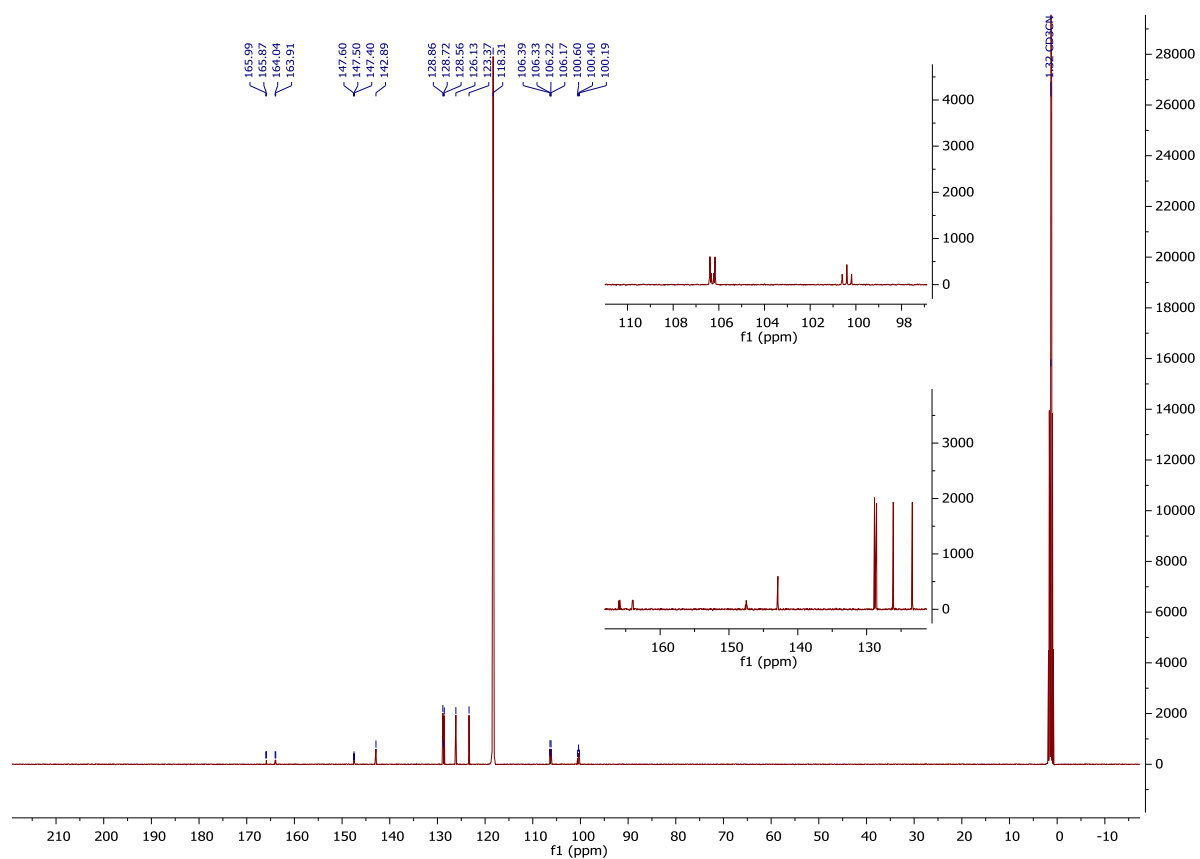


Figure S62: ^{13}C NMR spectrum of **8**.

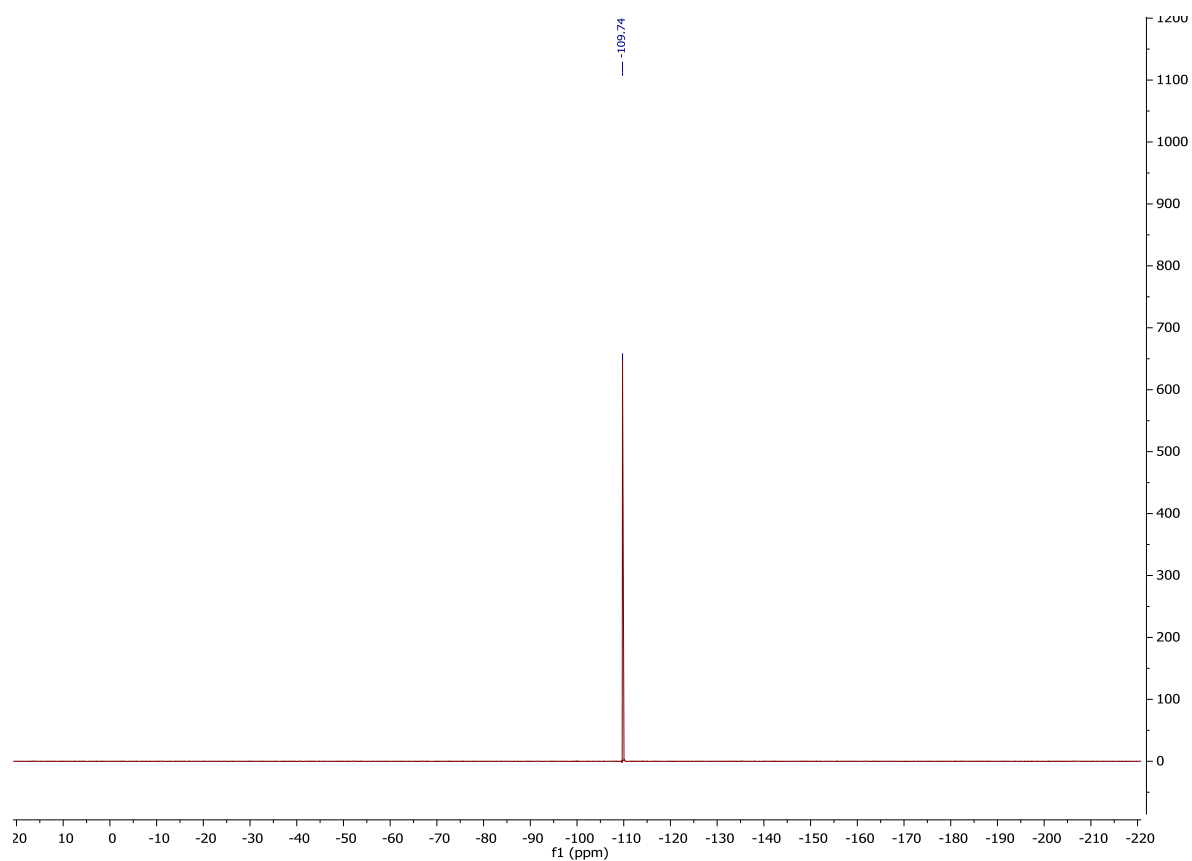


Figure S63: ^{19}F NMR spectrum of **8**.

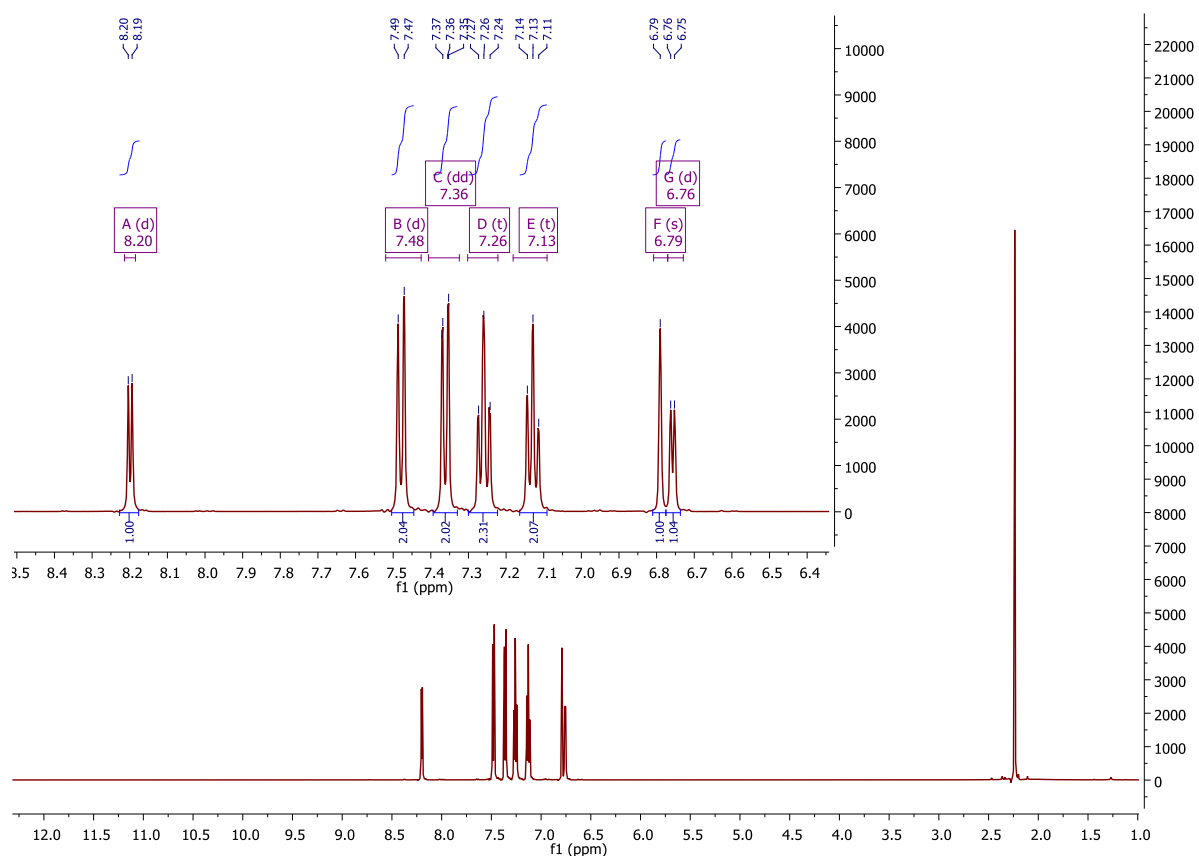


Figure S64: ¹H NMR spectrum of **9**.

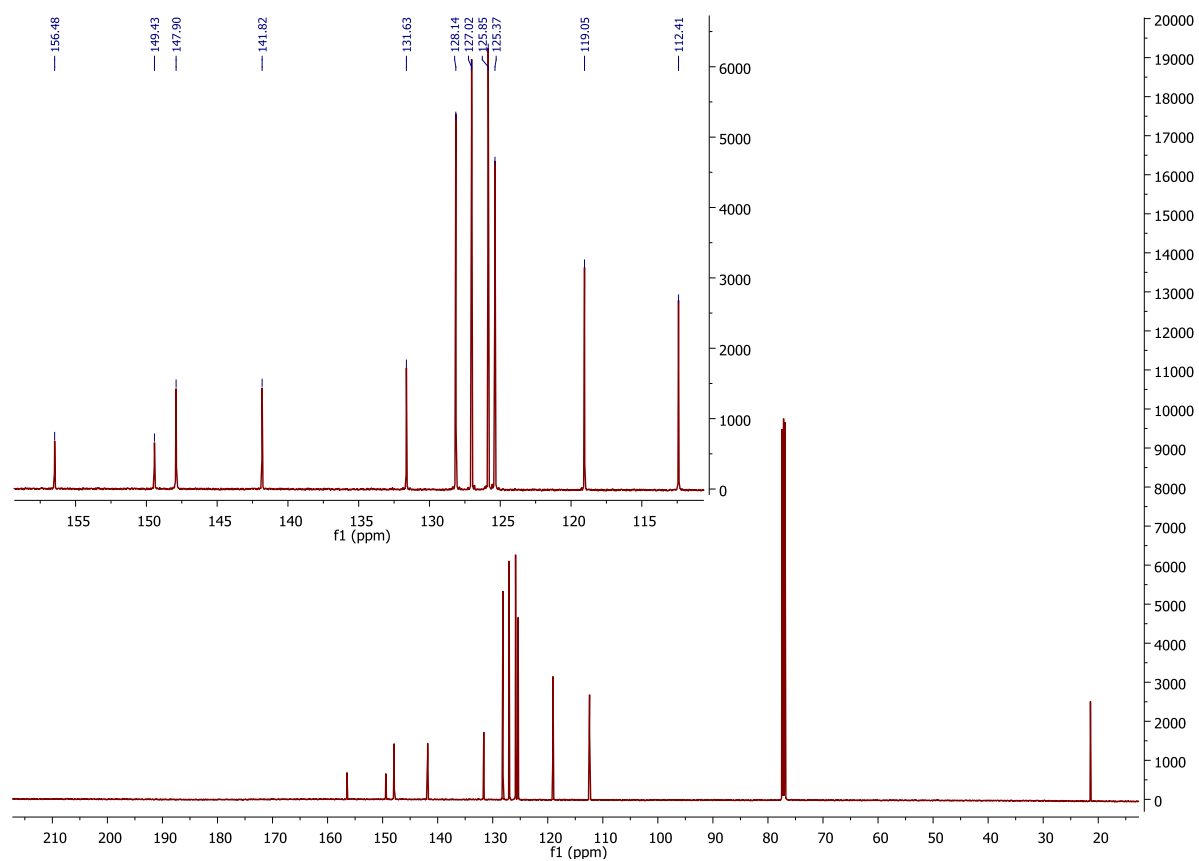


Figure S65: ¹³C NMR spectrum of **9**.

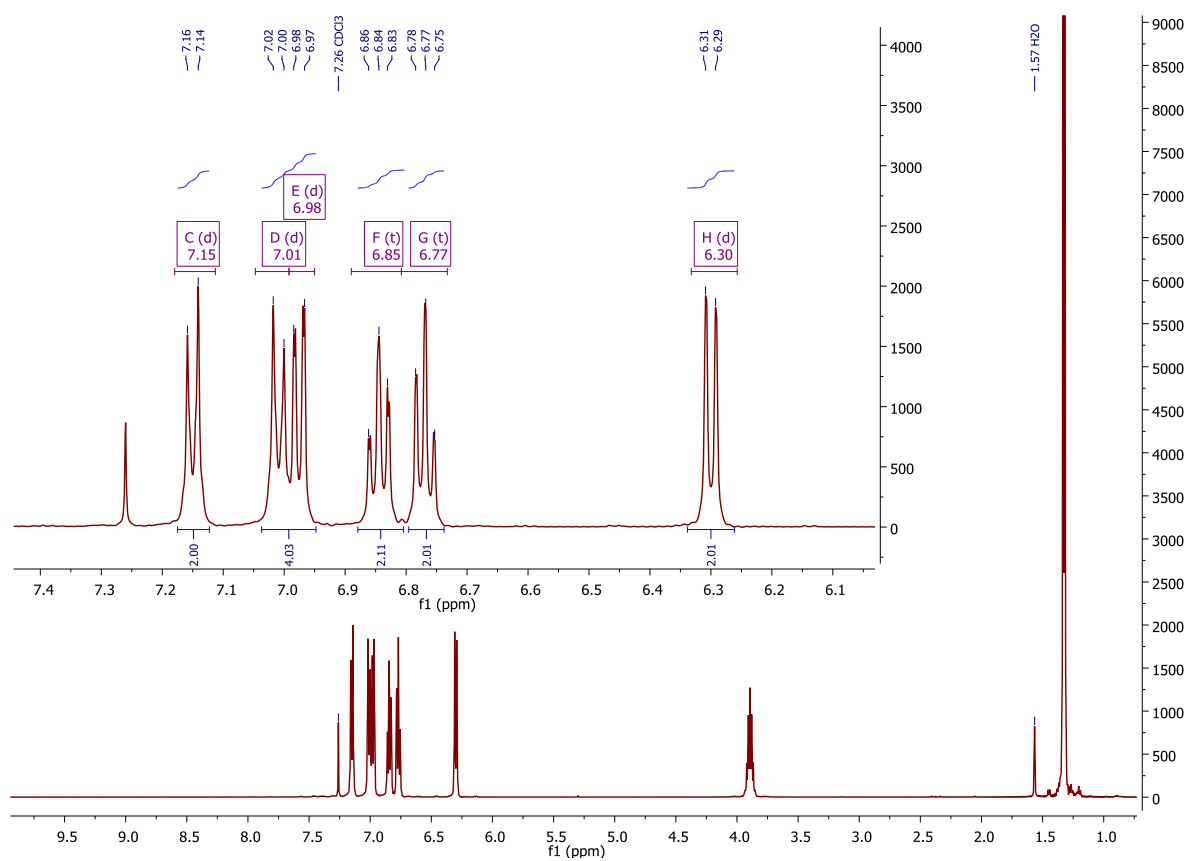


Figure S66: ^1H NMR spectrum of **10**.

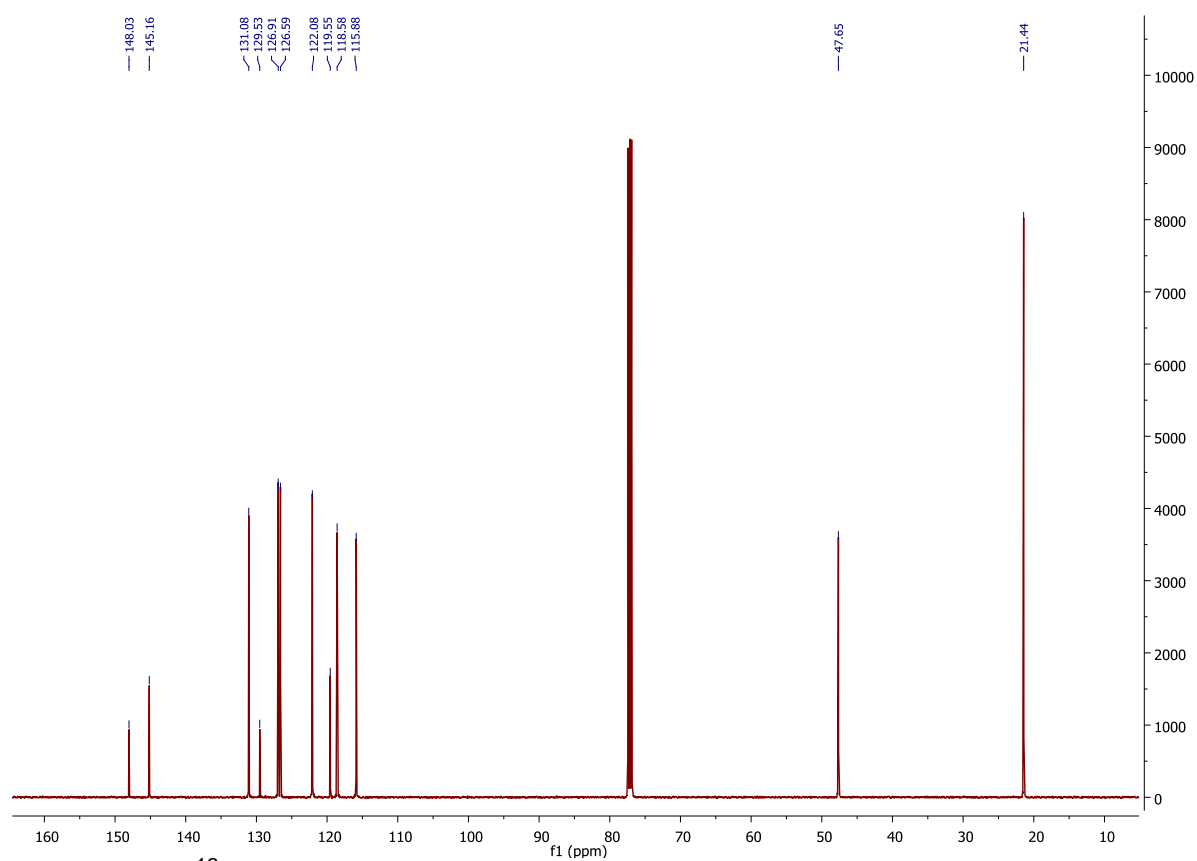


Figure S67: ¹³C NMR spectrum of **10**.

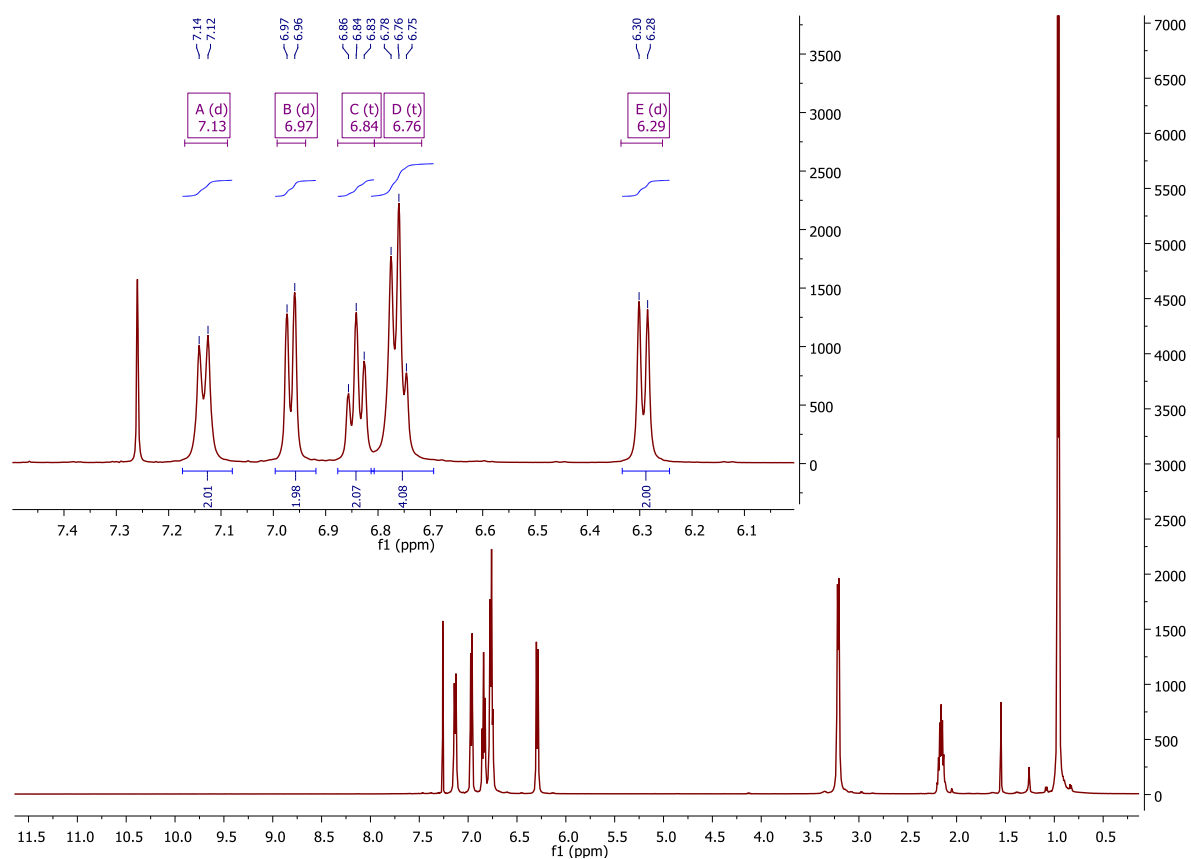


Figure S68: ^1H NMR spectrum of **11**.

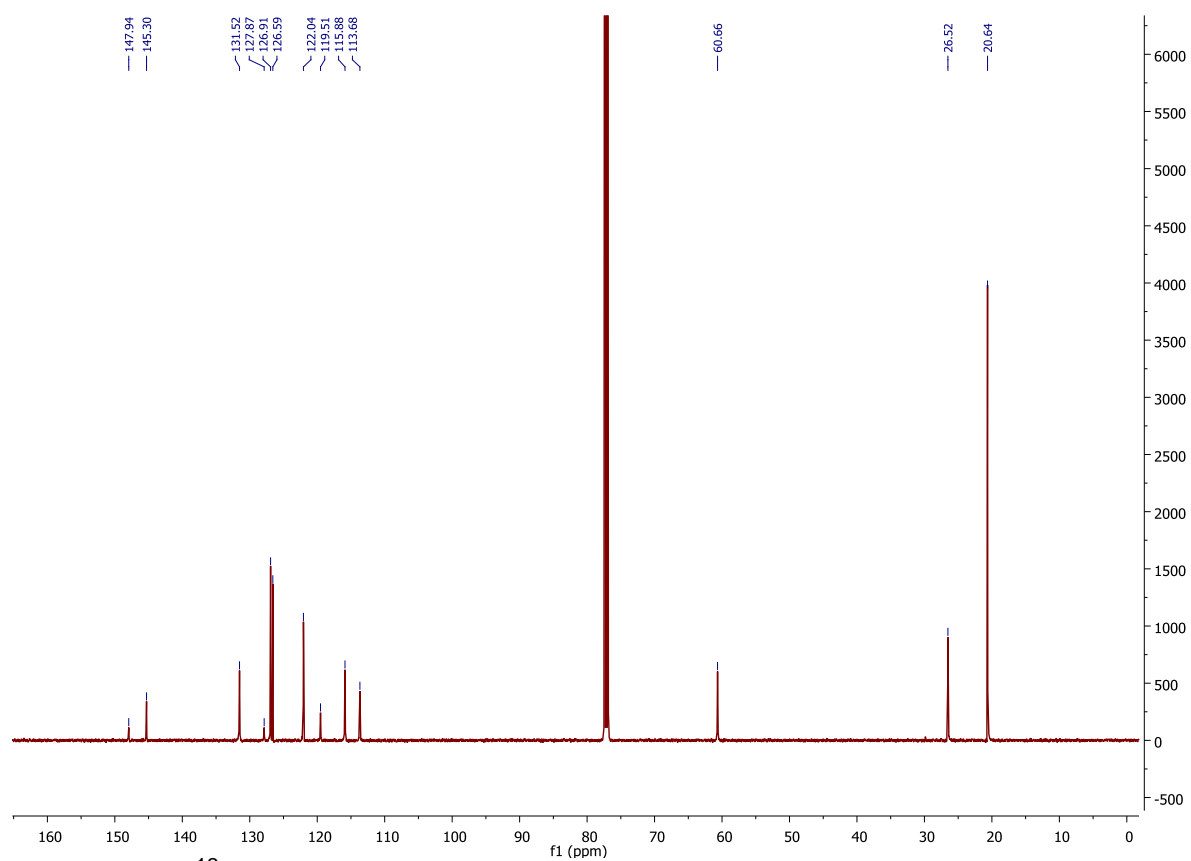


Figure S69: ¹³C NMR spectrum of **11**.

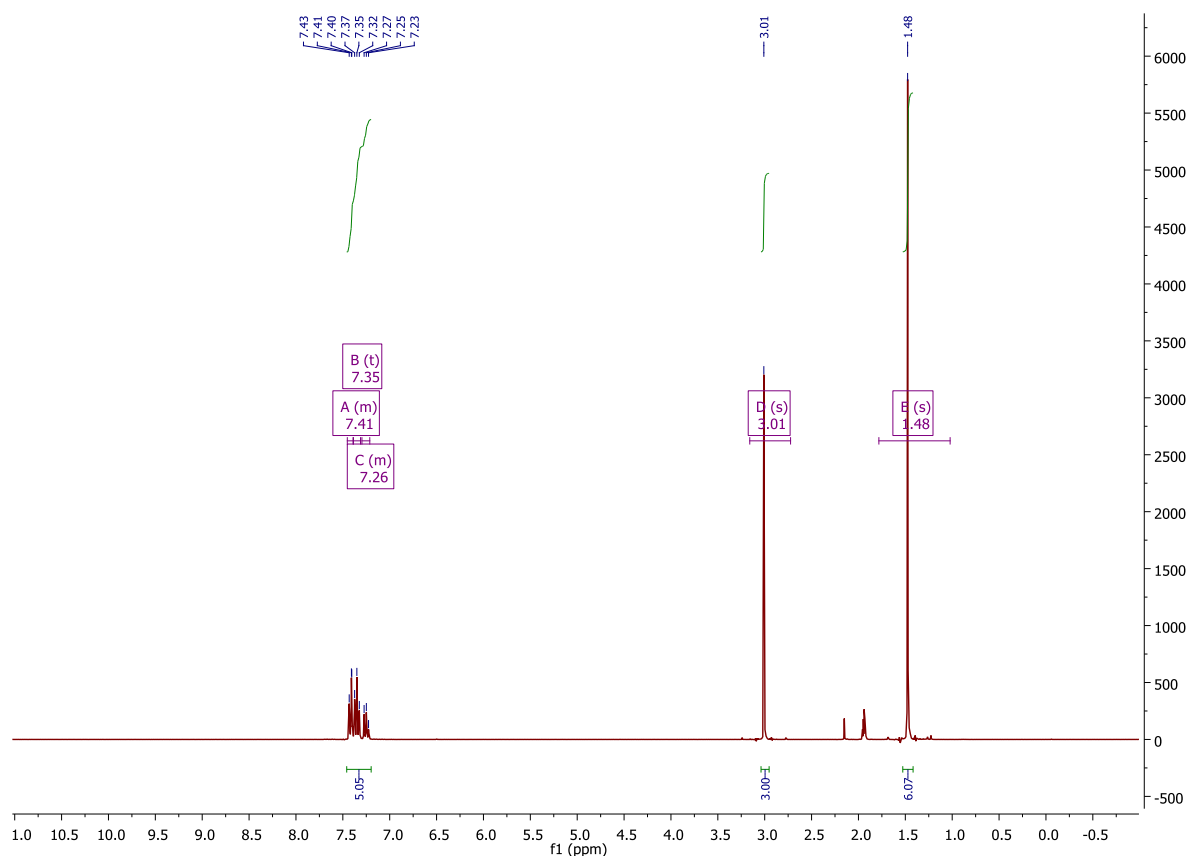


Figure S70: ¹H NMR spectrum of **16**.

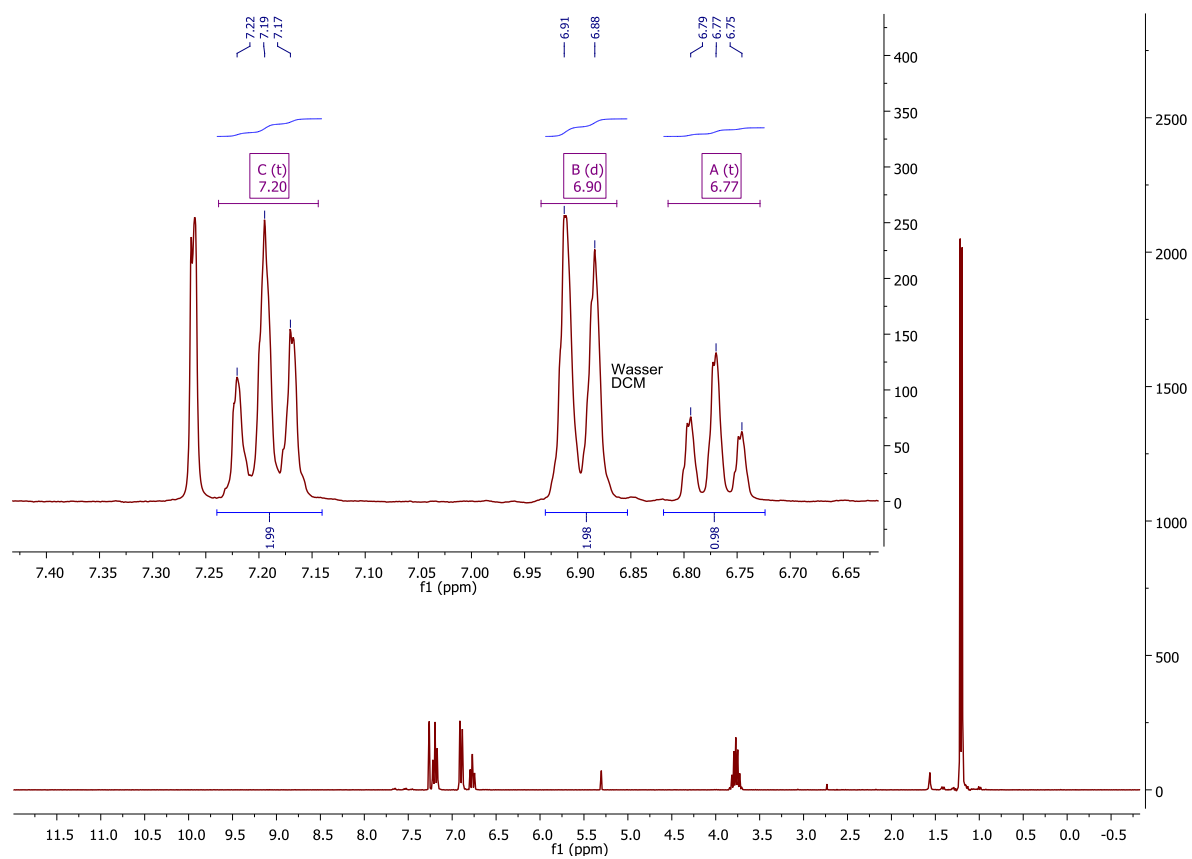


Figure S71: ¹H NMR spectrum of **17**.

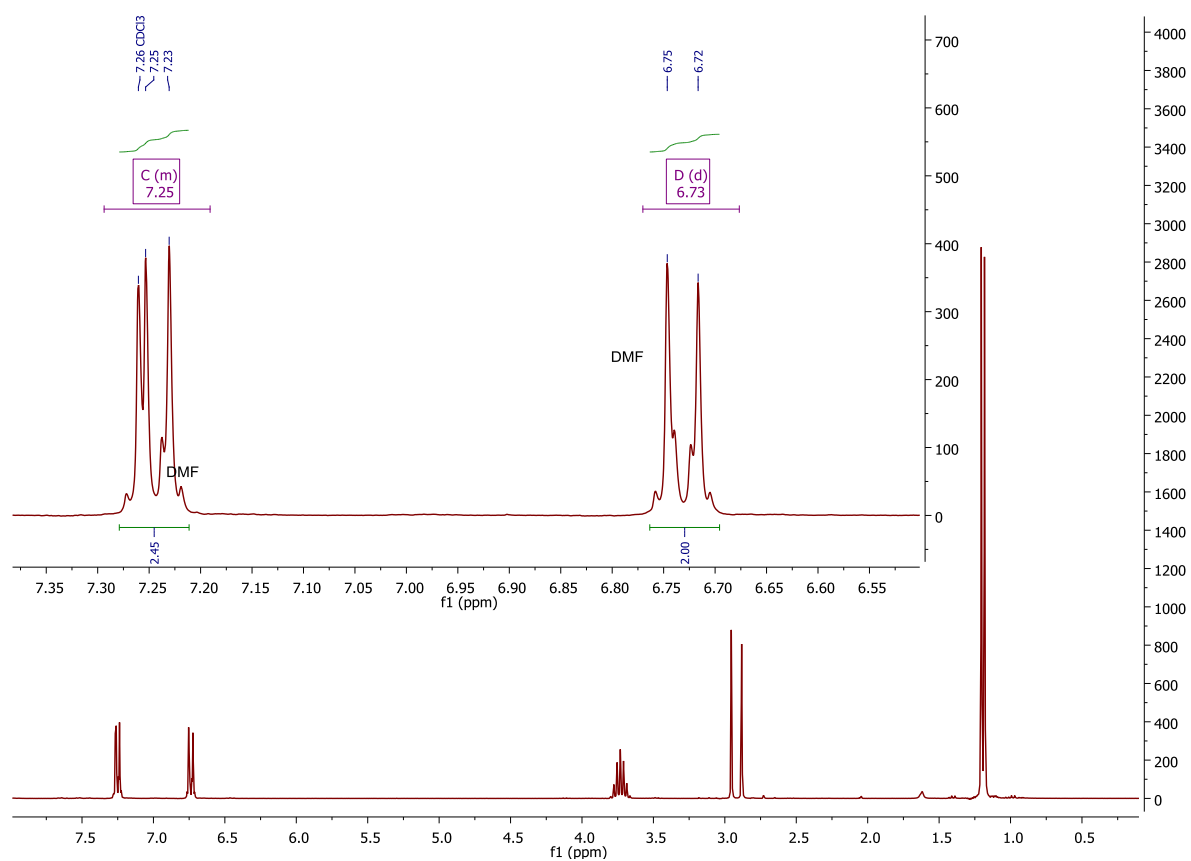


Figure S72: ^1H NMR spectrum of **18**.

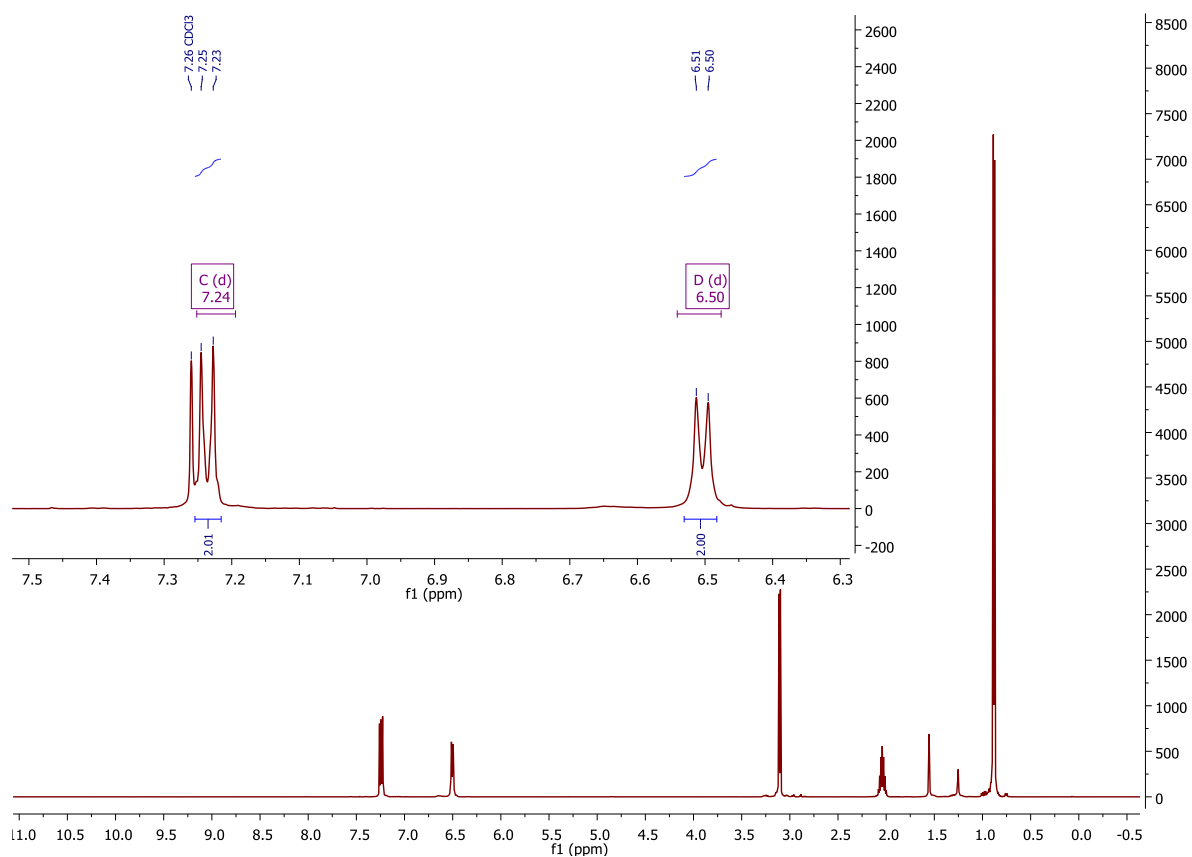


Figure S73: ^1H NMR spectrum of **19**.

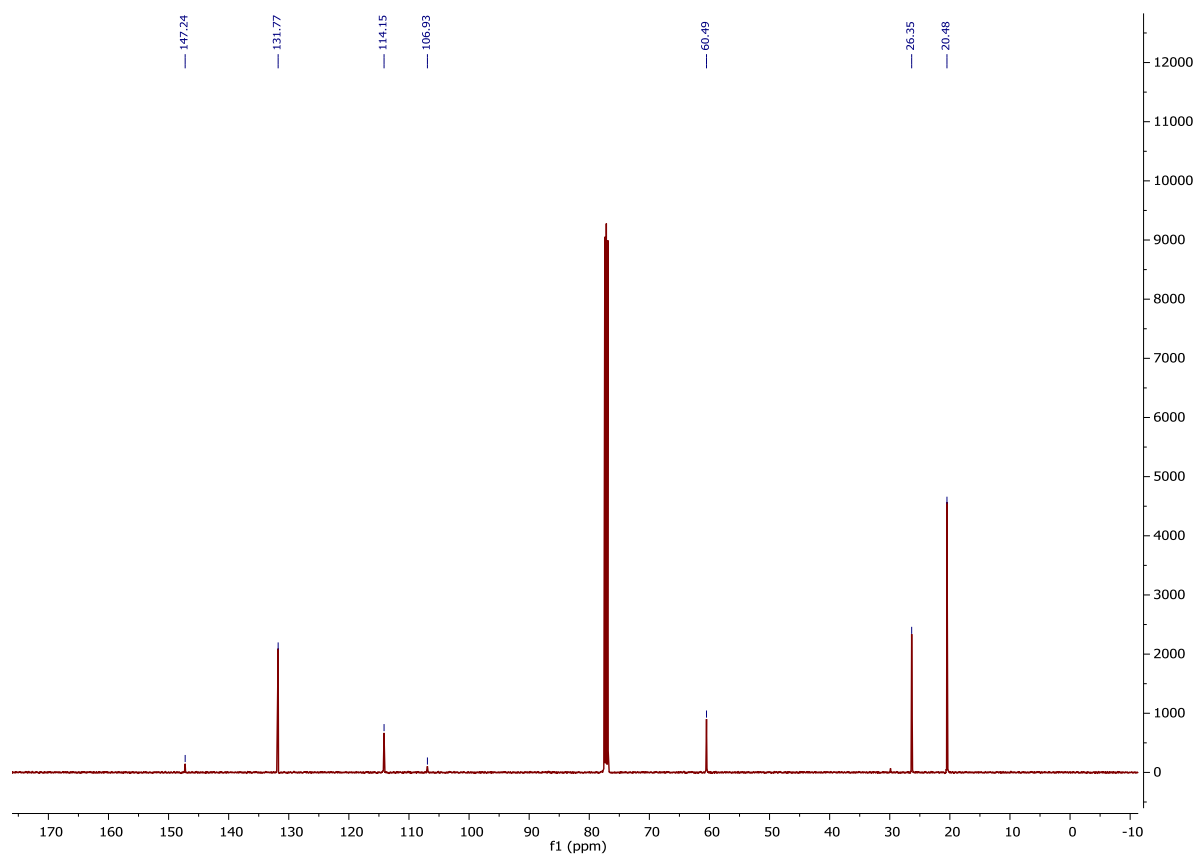
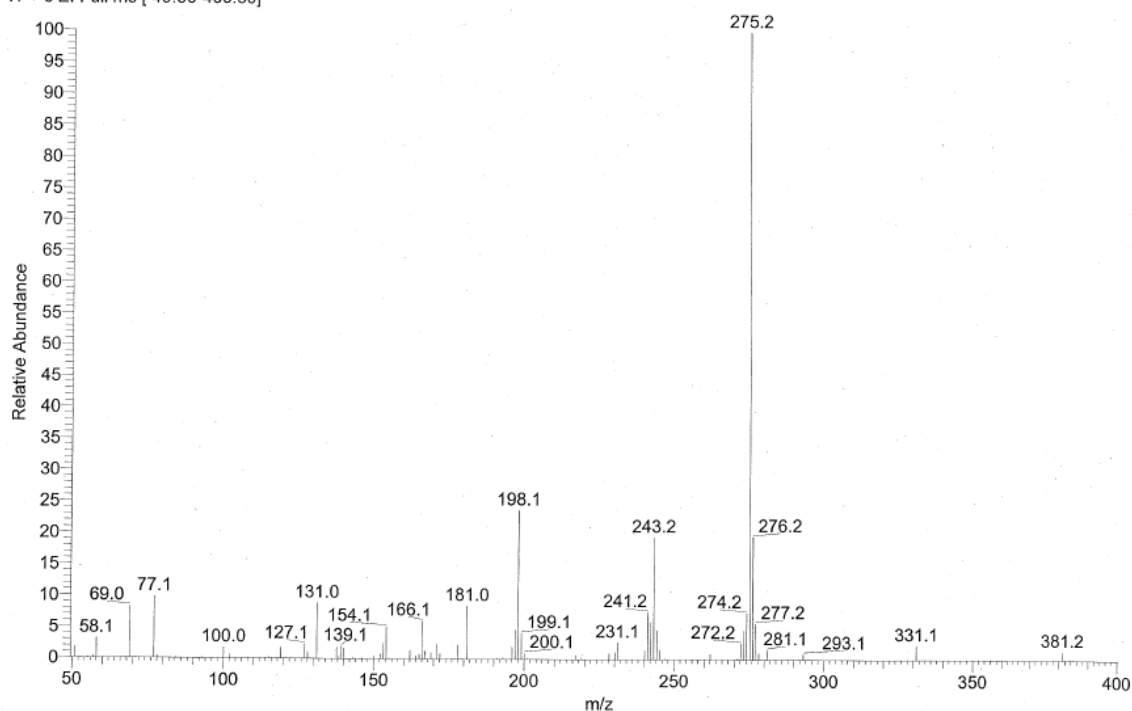


Figure S74: ^{13}C NMR spectrum of **19**.

Mass spectrometric data

MAT 95, +EI, Que 110, dir offen 1/24/2018 9:23:36 AM PTA-630
mpe D. Rombach AK Wagenknecht
pta630 #2-4 RT: 0.23-0.39 AV: 3 NL: 4.46E5
T: + c EI Full ms [49.50-400.50]



1/24/2018 9:26:28 AM

pta630-c1 #2 RT: 0.23 AV: 1 NL: 4.02E5
T: + c EI Full ms [49.50-400.50]

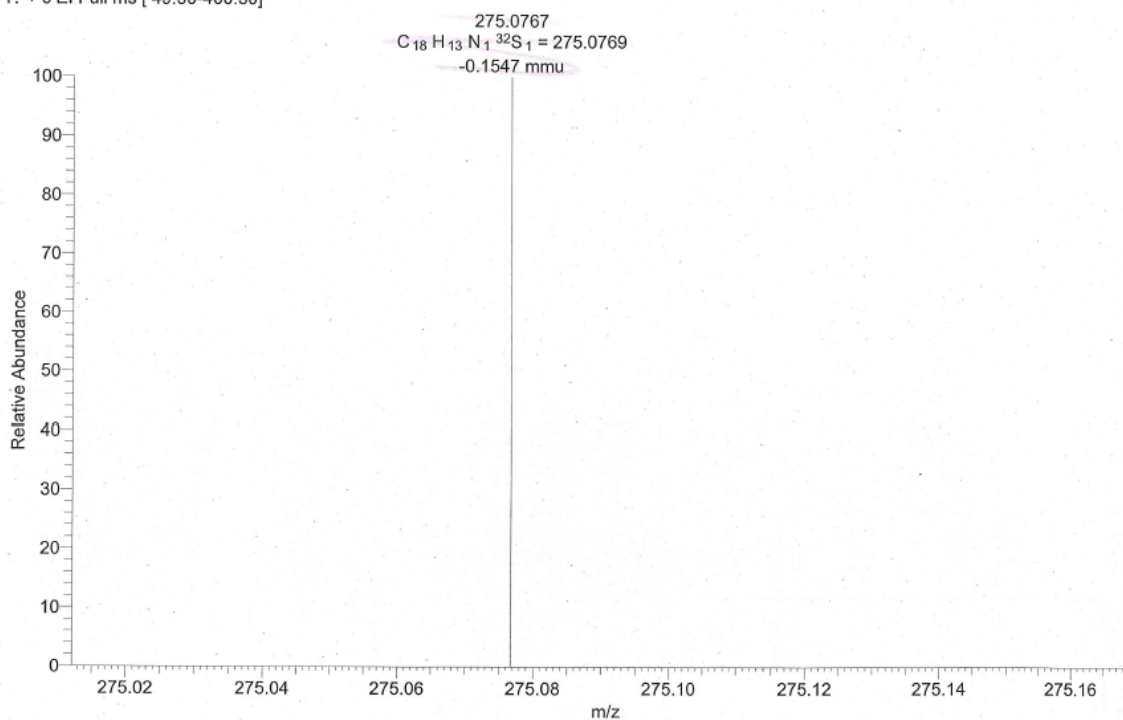


Figure S75: HR-EI/MS of 1.

Confidence

Data: FS_003_2_ATT_0001.D23[c] 8 May 2017 11:24 Cal: AK Braese Pep_Bruker 5 May 2017 18:39

Shimadzu Biotech Axima Confidence 2.9.3.20110624: Mode Reflectron, Power: 51, Blanked, P.Ext. @ 200 (bin 59)

%Int. 36 mV[sum= 3566 mV] Profiles 1-100 Smooth Gauss 10 -Baseline 30

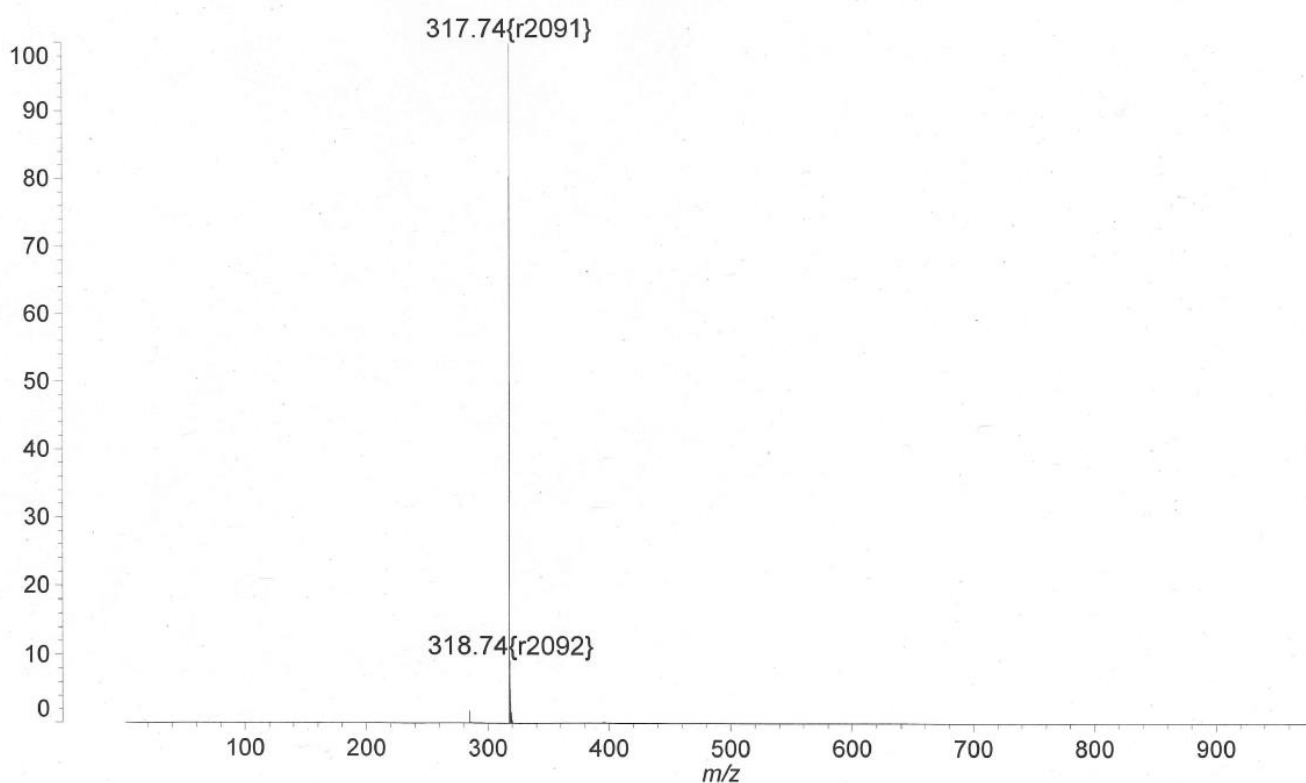


Figure S76: MALDI-TOF-MS of 2..

Confidence

Data: FS_007_ATT_0002.N16[c] 22 May 2017 11:35 Cal: AK Braese Pep_Bruce. 24 Oct 2017 16:46

Shimadzu Biotech Axima Confidence 2.9.3.20110624: Mode Reflectron, Power: 88, Blanked, P.Ext. @ 500 (bin 59)

%Int. 569 mV[sum= 26194 mV] Profiles 1-46 Smooth Gauss 2 -Baseline 6

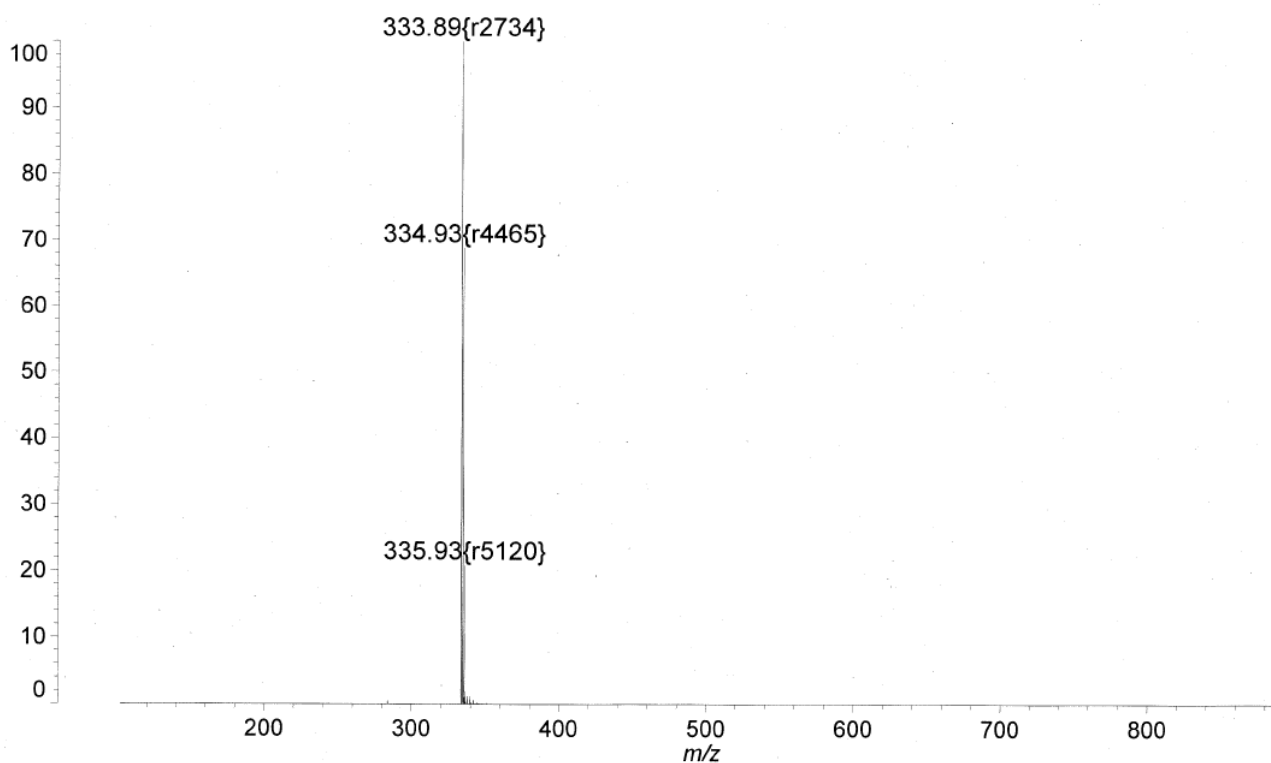


Figure S77: MALDI-TOF-MS of **3**.

Confidence

Data: FS_011_ATT_0001.N22[c] 22 May 2017 11:39 Cal: AK Braese Pep_Bruce. 24 Oct 2017 16:46

Shimadzu Biotech Axima Confidence 2.9.3.20110624: Mode Reflectron, Power: 79, Blanked, P.Ext. @ 500 (bin 59)

%Int. 74 mV[sum= 5300 mV] Profiles 1-72 Smooth Gauss 2 -Baseline 6

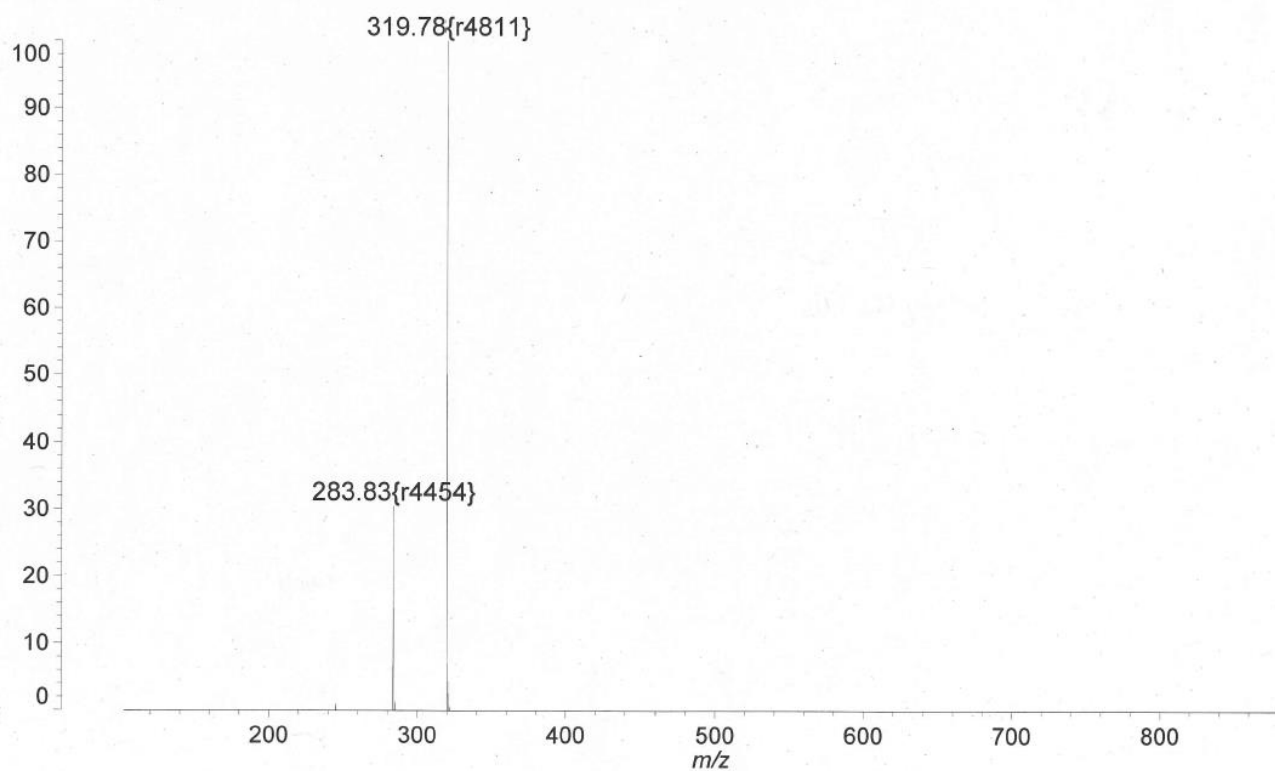


Figure S78: MALDI-TOF-MS of **4**.

Confidence

Data: FS_004_ATT_0001.J21[c] 3 May 2017 14:44 Cal: AK Braese Pep_Bruker 2 May 2017 16:10

Shimadzu Biotech Axima Confidence 2.9.3.20110624: Mode Reflectron, Power: 67, Blanked, P.Ext. @ 280 (bin 59)

%Int. 1369 mV[sum= 136949 mV] Profiles 1-100 Smooth Av 10 -Baseline 30

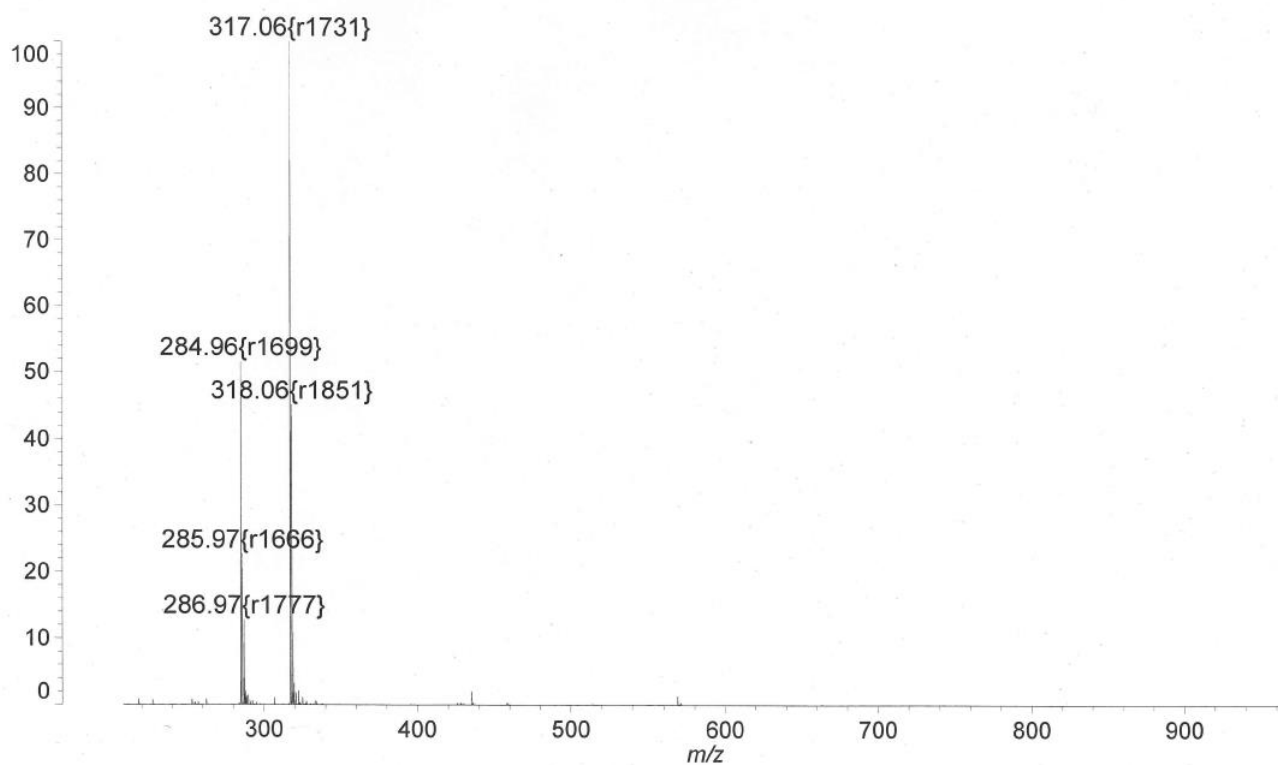
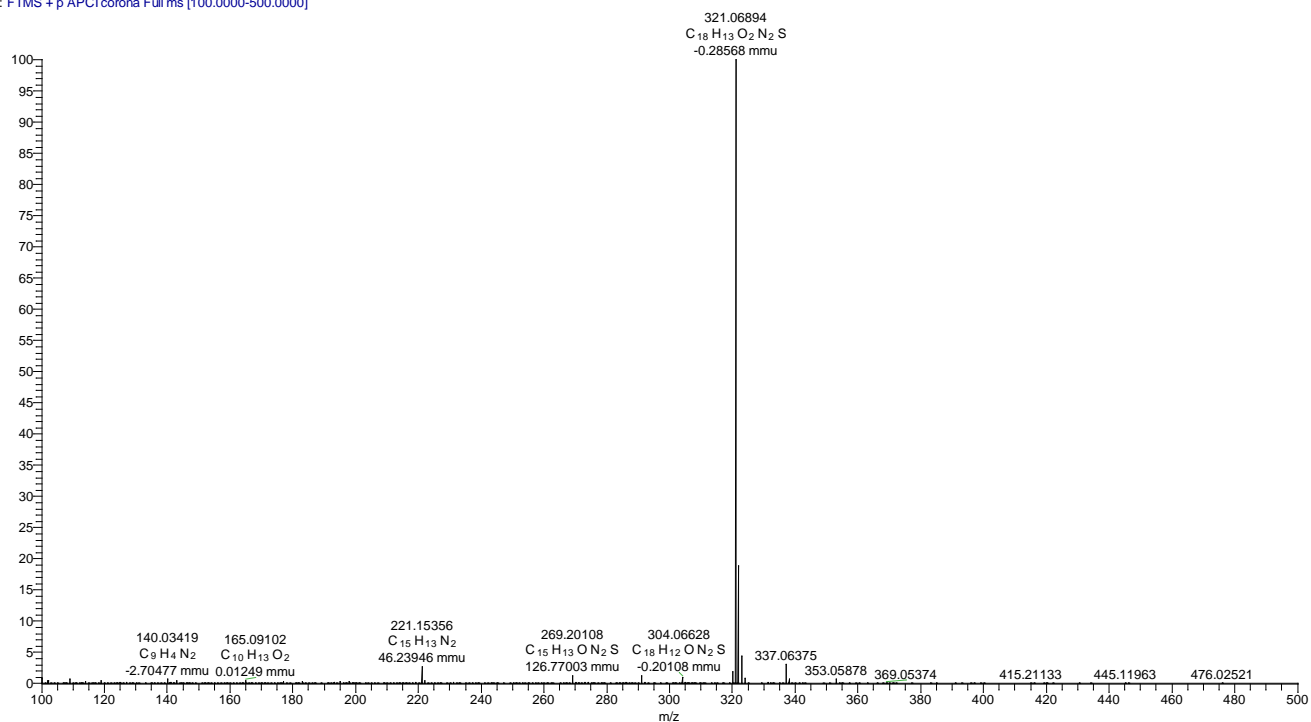


Figure S79: MALDI-TOF-MS of **5**.

FS 026 #5 RT: 0.09 AV: 1 NL: 5.22E9
T: FTMS + p APCI corona Full ms [100.0000-500.0000]



FS 026.1 #7 RT: 0.12 AV: 1 NL: 2.61E9
T: FTMS + p APCI corona SIM ms [300.0000-350.0000]

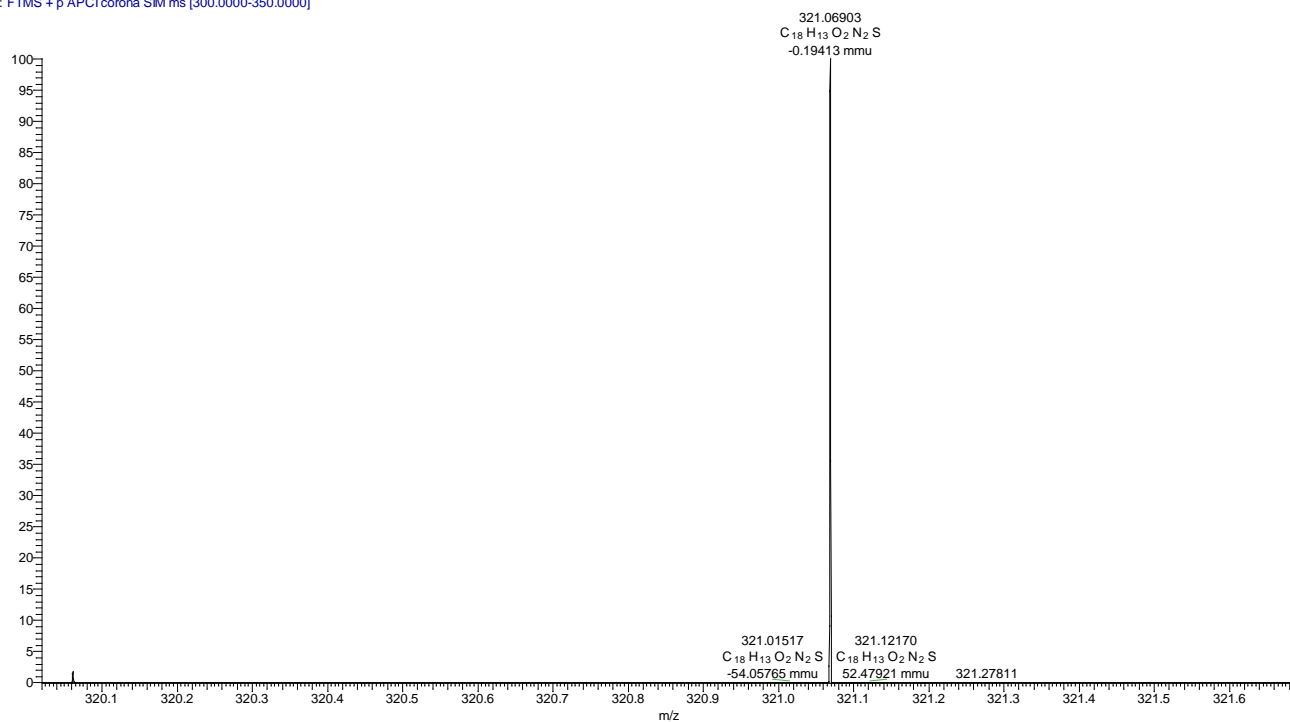


Figure S80: HR-APCI-MS of 6.

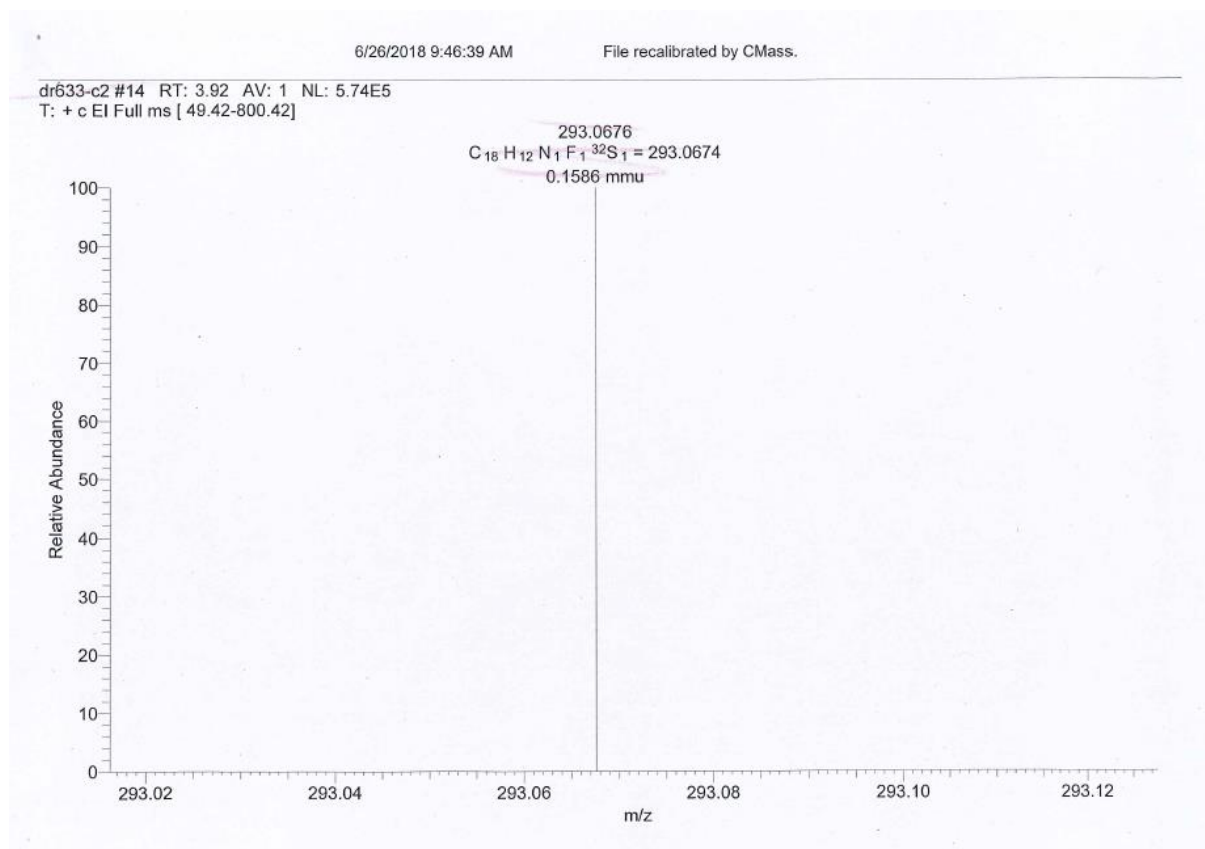
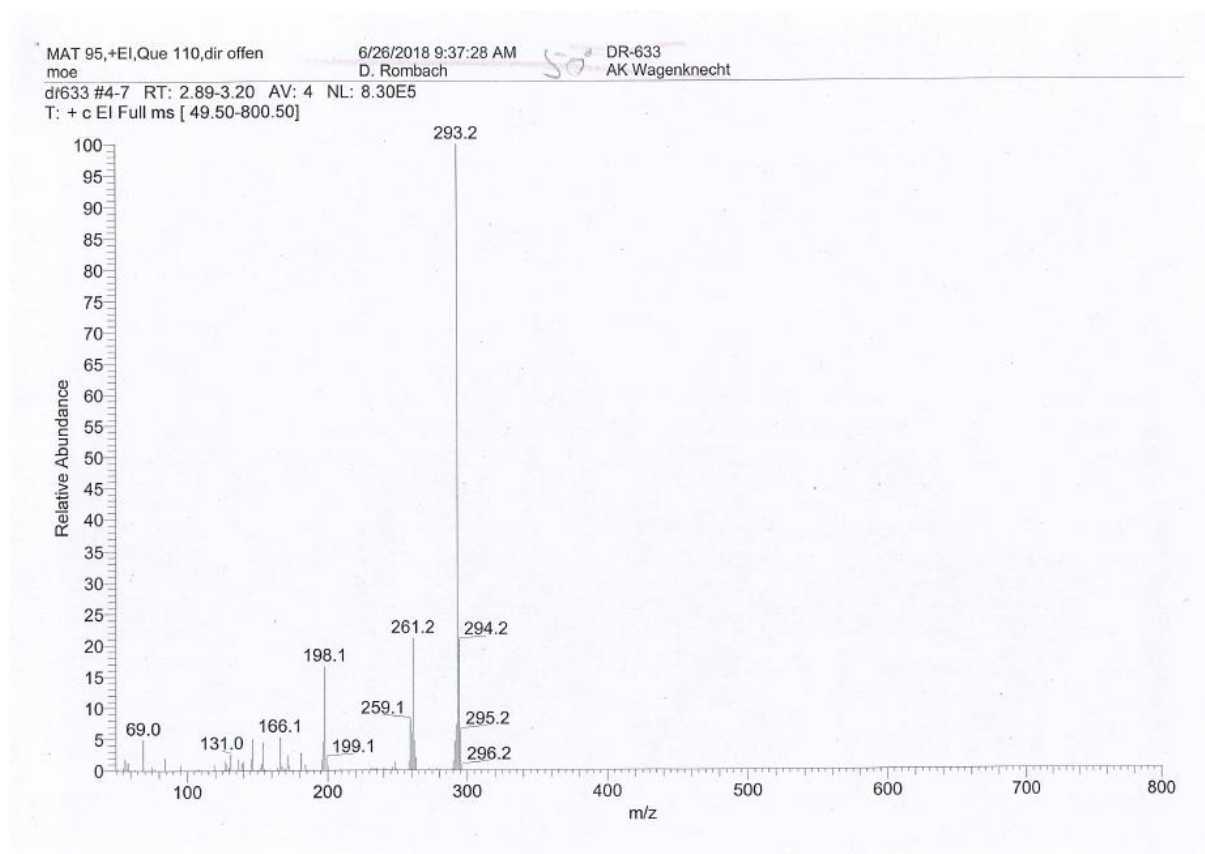


Figure S81: HR-EI-MS of 7.

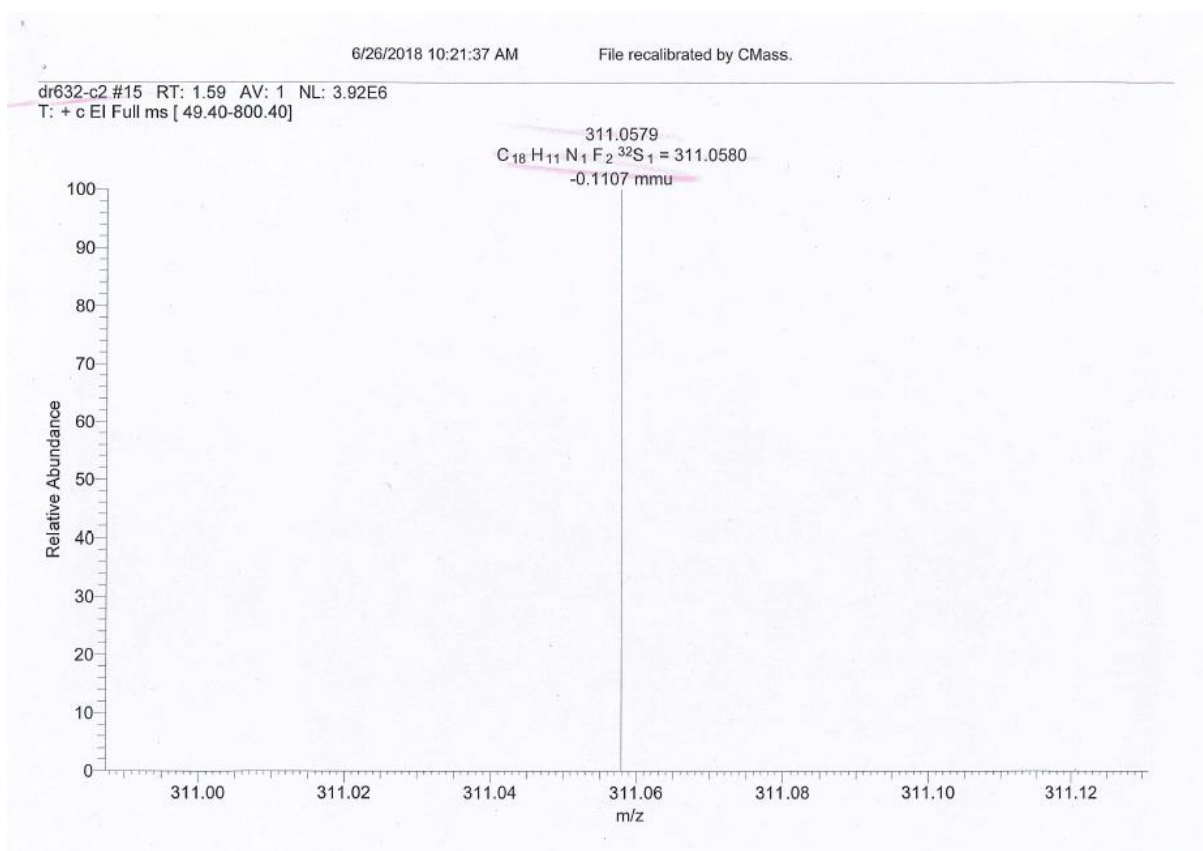
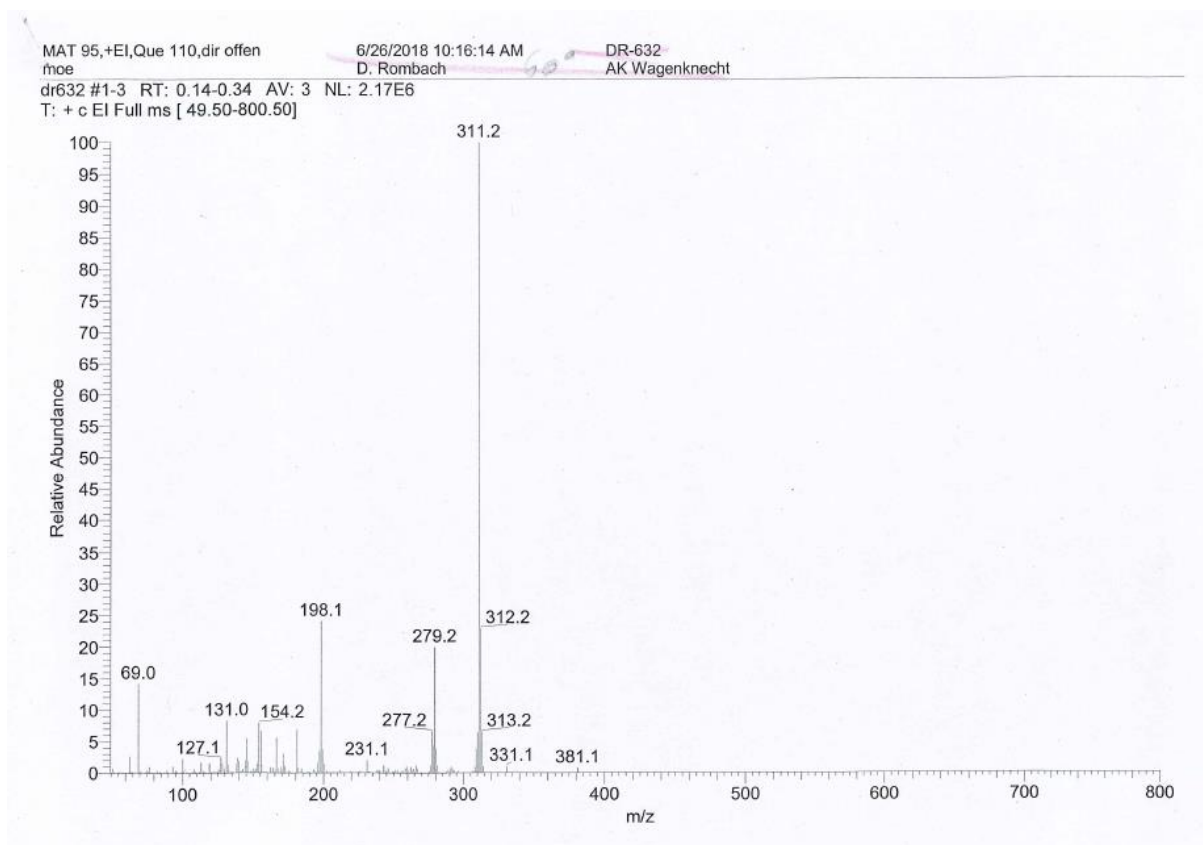


Figure S82: HR-EI-MS of 8.

Confidence

Data: FS_009_ATT_0001.N17[c] 22 May 2017 11:35 Cal: AK Braese Pep_Bruker, 24 Oct 2017 16:46

Shimadzu Biotech Axima Confidence 2.9.3.20110624: Mode Reflectron, Power: 88, Blanked, P.Ext. @ 500 (bin 59)

%Int. 1328 mV[sum= 17259 mV] Profiles 1-13 Smooth Gauss 2 -Baseline 6

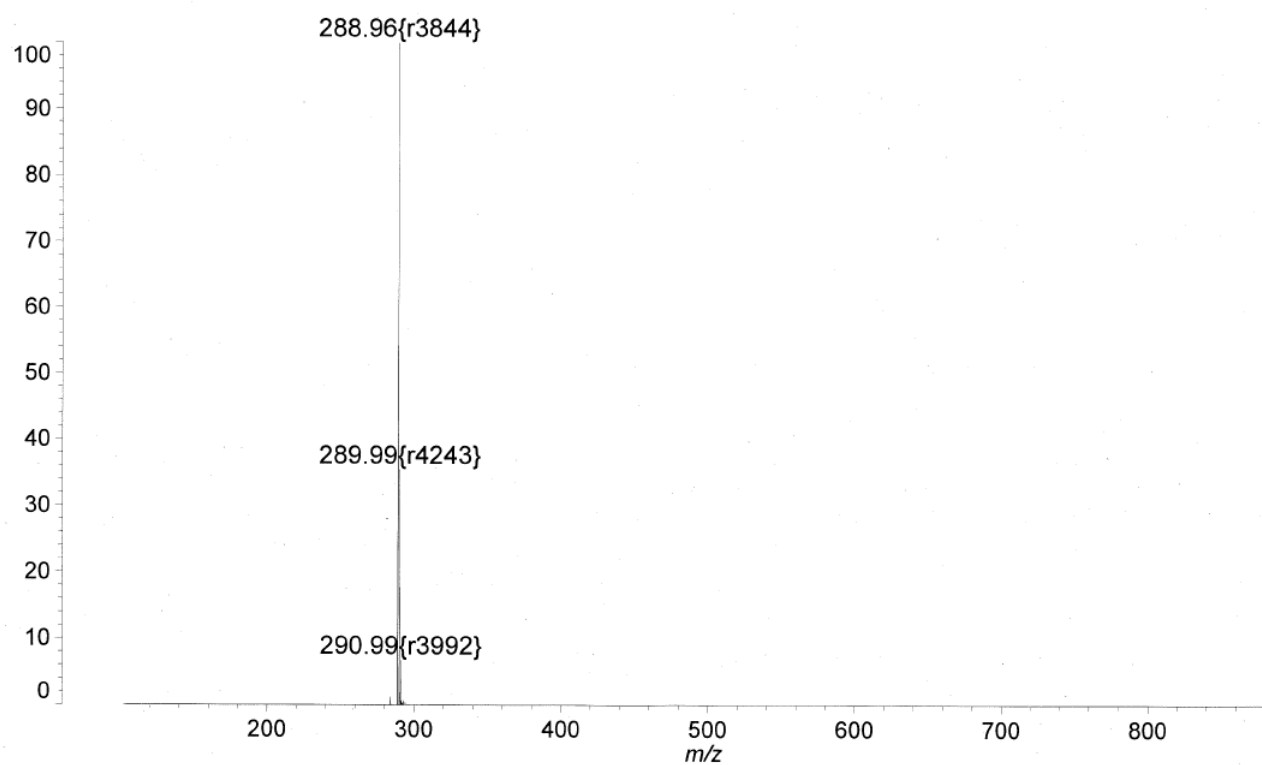


Figure S83: MALDI-TOF-MS of **9**.

Confidence

Data: FS_029_ATT_0001.N18[c] 22 May 2017 11:36 Cal: AK Braese Pep_Bruke. 24 Oct 2017 16:46

Shimadzu Biotech Axima Confidence 2.9.3.20110624: Mode Reflectron, Power: 84, Blanked, P.Ext. @ 500 (bin 59)

%Int. 939 mV[sum= 15027 mV] Profiles 1-16 Smooth Gauss 2 -Baseline 6

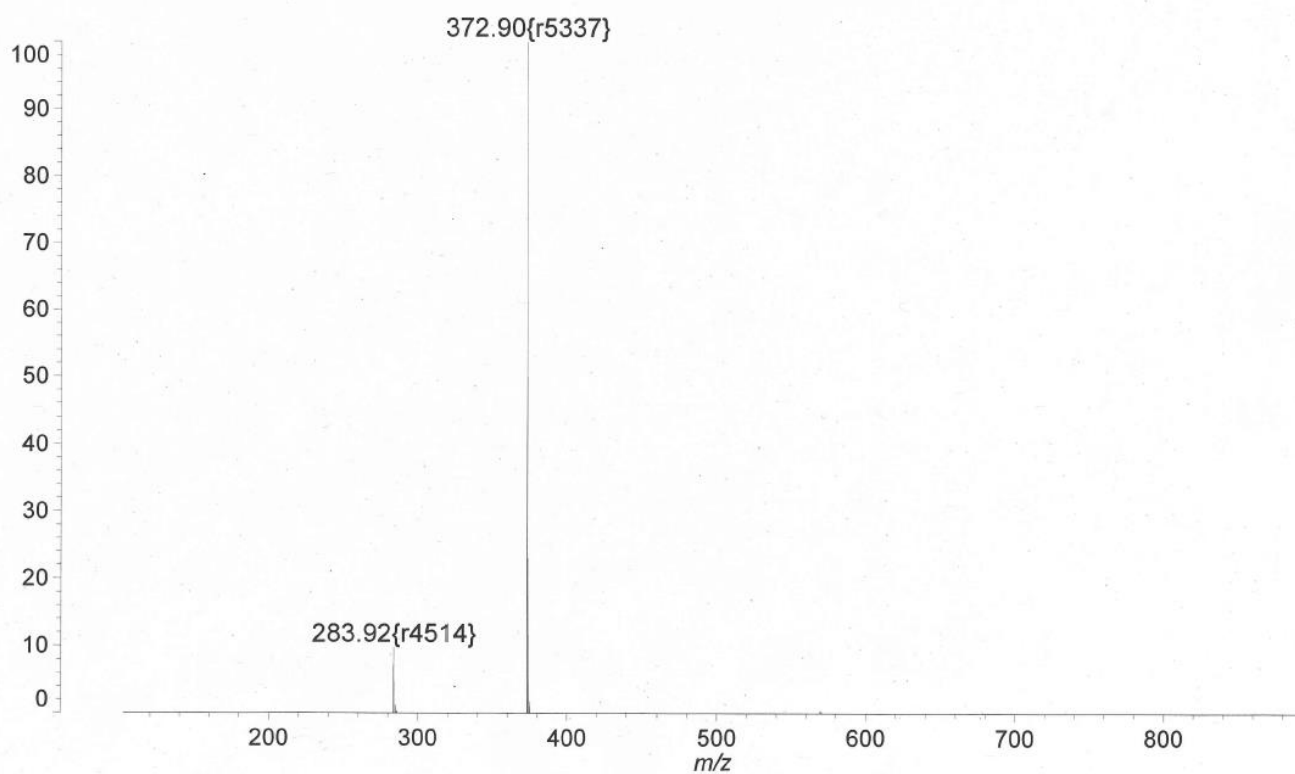
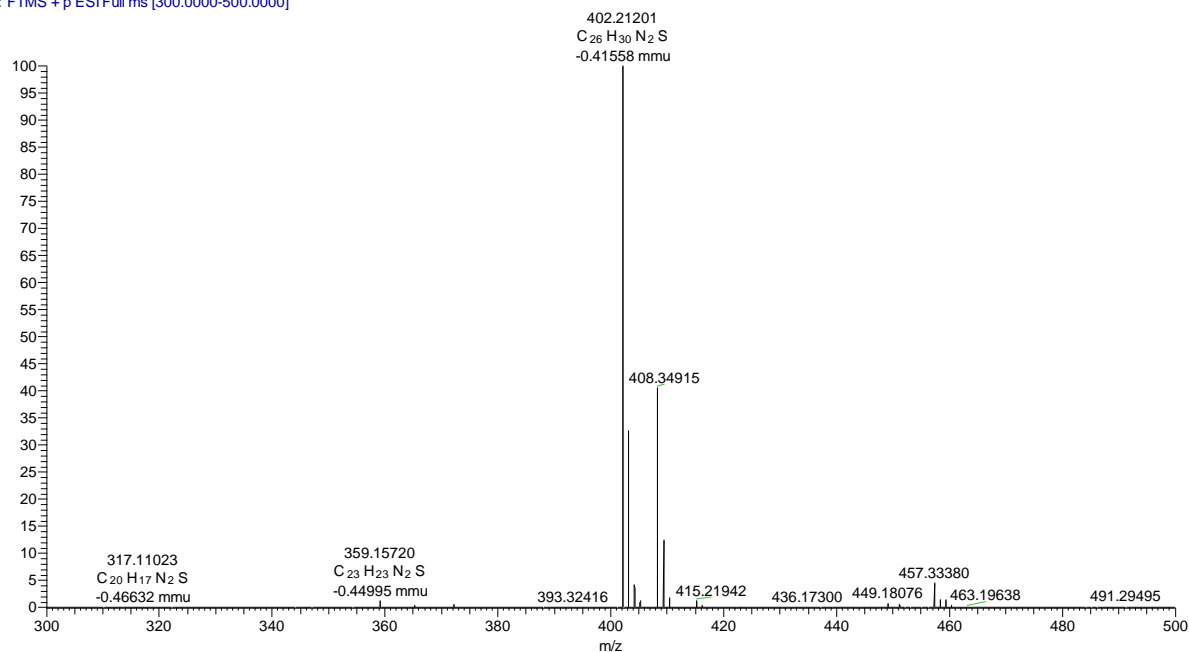


Figure S84: MALDI-TOF-MS of 10.

FS 031 #1 RT: 0.02 AV: 1 NL: 3.35E9
T: FTMS + p ESI Full ms [300.0000-500.0000]



FS 031 #1 RT: 0.02 AV: 1 NL: 3.35E9
T: FTMS + p ESI Full ms [300.0000-500.0000]

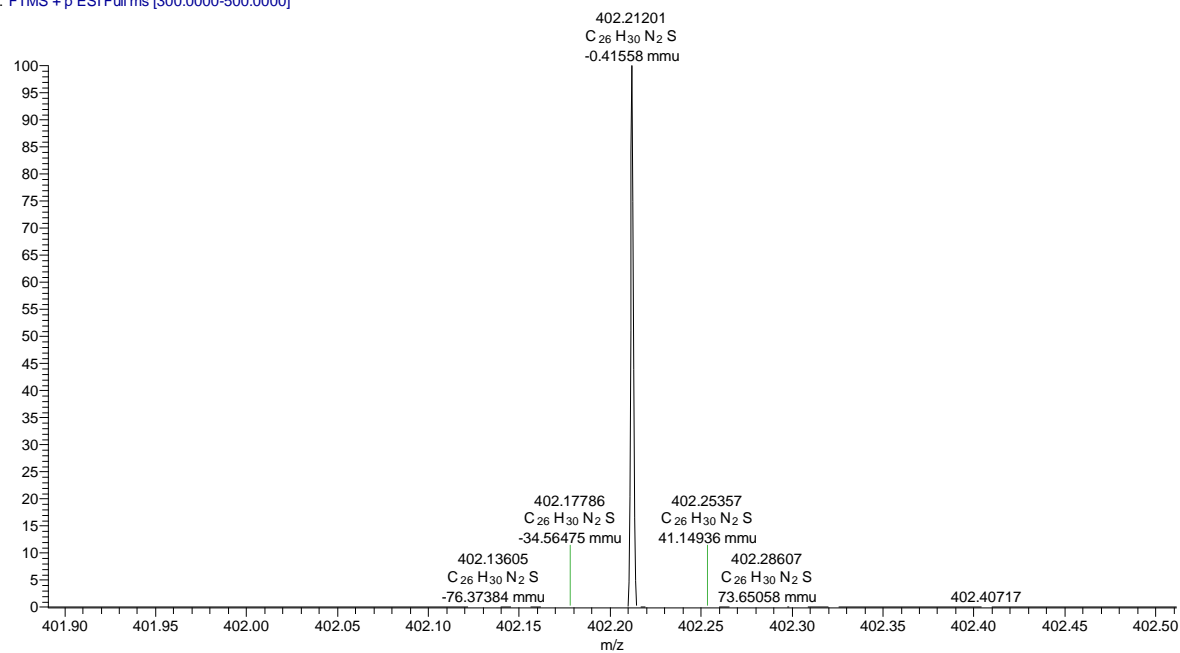
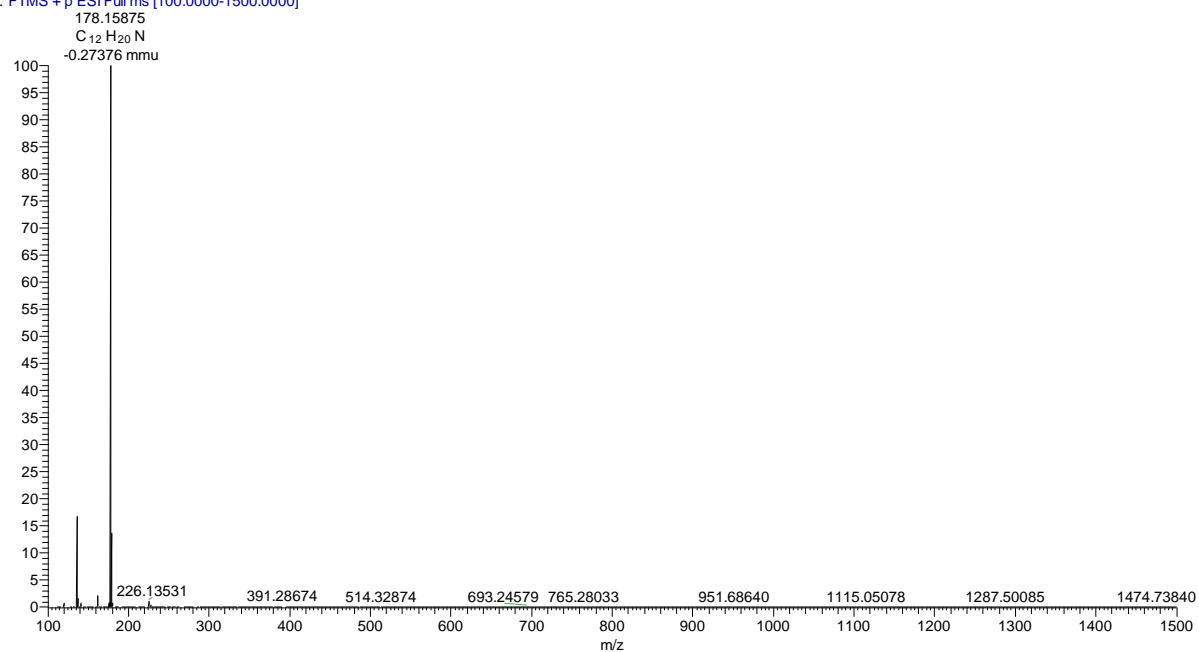


Figure S85: HR-ESI-MS of 11.

FS028 #1 RT: 0.02 AV: 1 NL: 6.42E9
T: FTMS + p ESI Full ms [100.0000-1500.0000]



FS028 #1 RT: 0.02 AV: 1 NL: 6.42E9
T: FTMS + p ESI Full ms [100.0000-1500.0000]

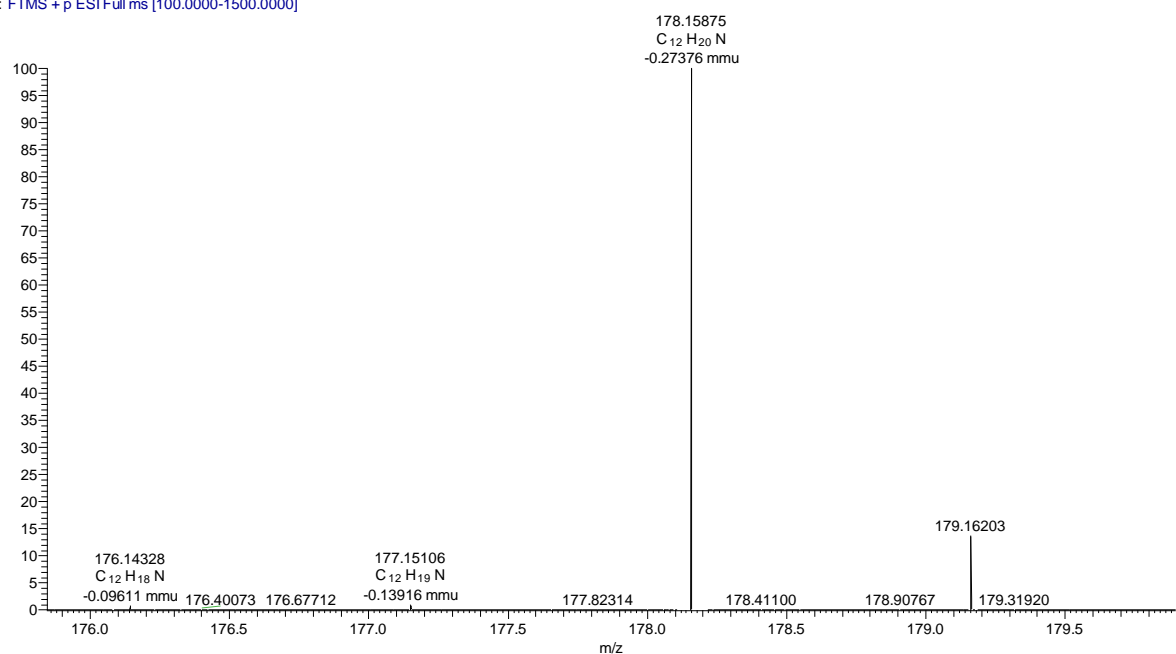


Figure S86: HR-ESI-MS of 17.

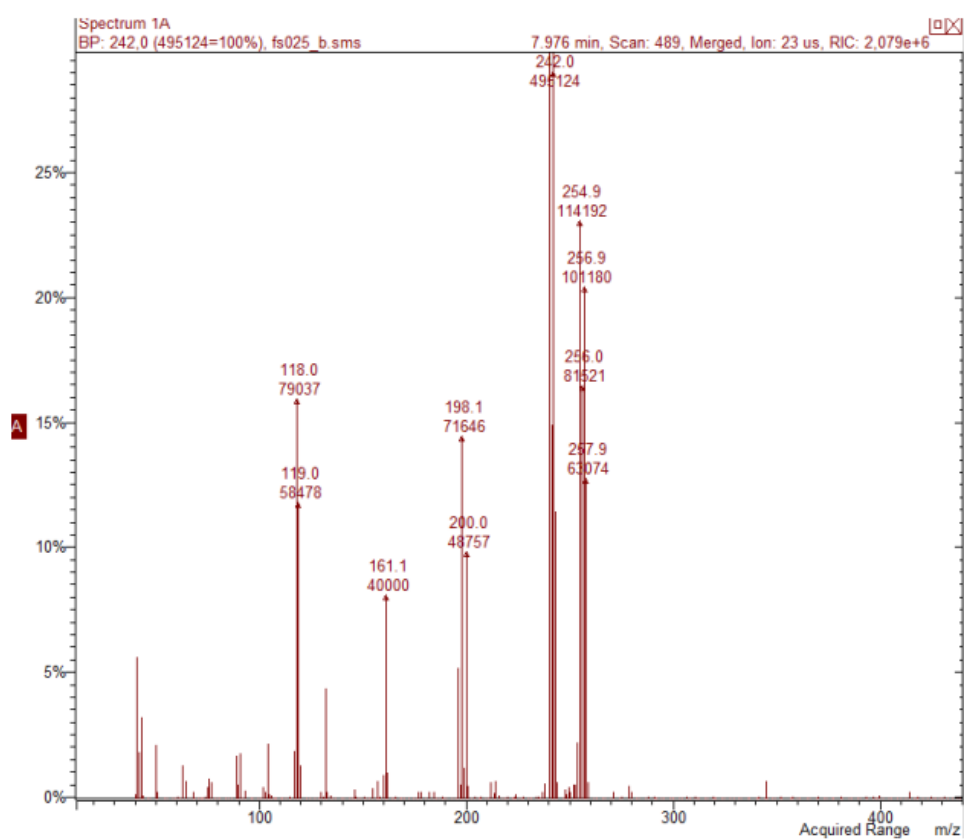
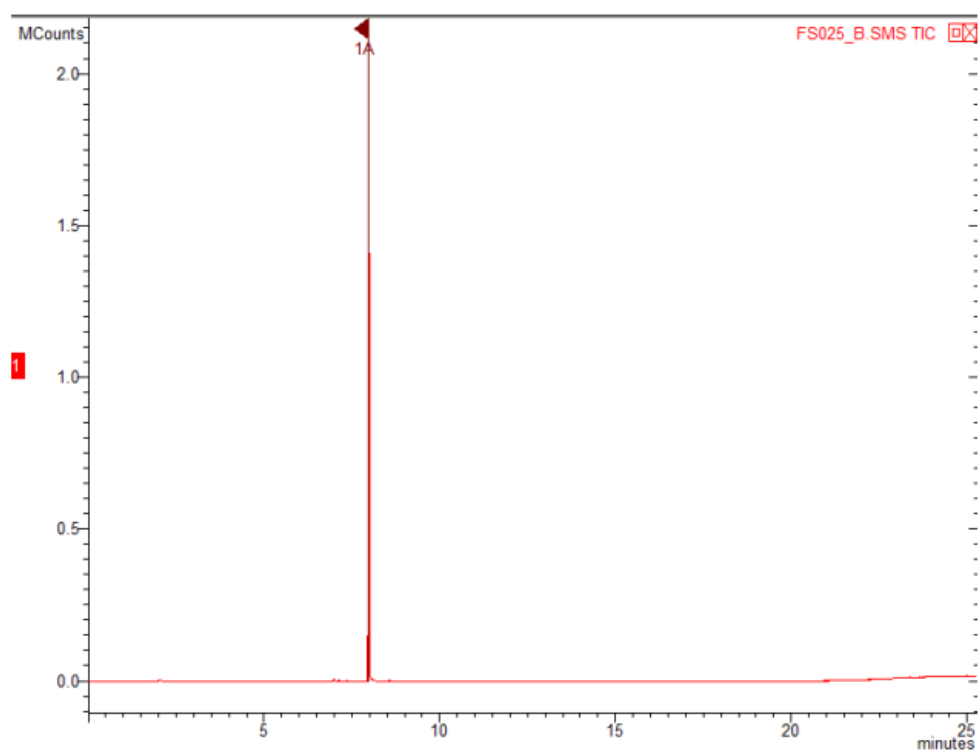
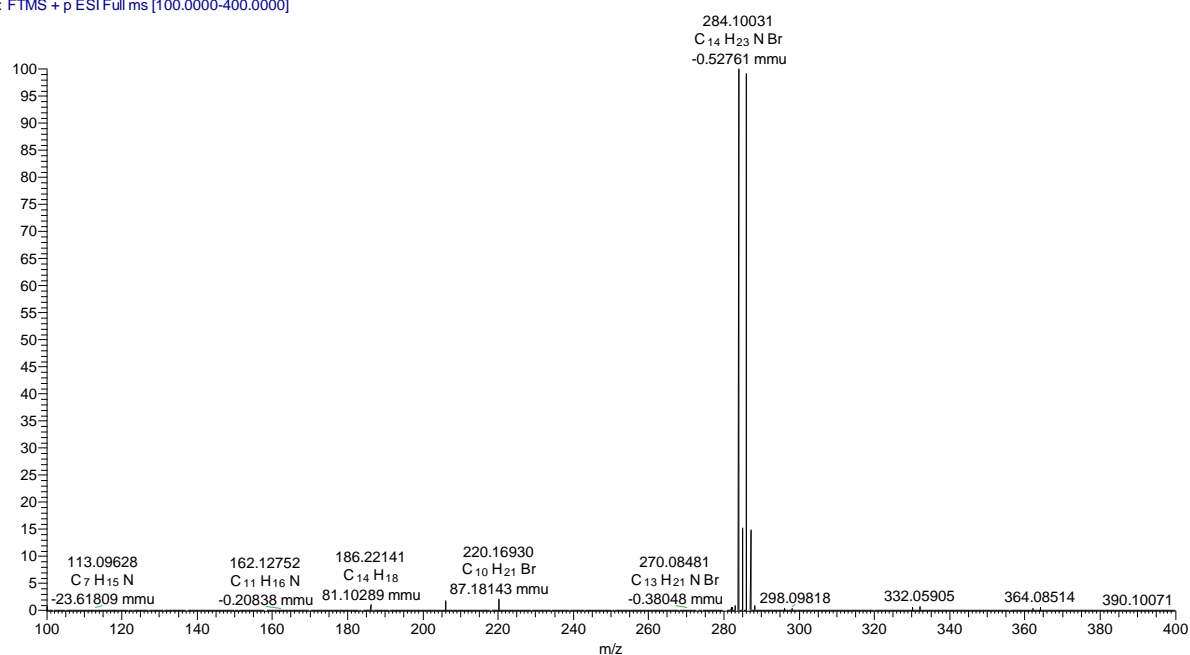


Figure S87: GC-EI-MS of 18.

FS 030 #1 RT: 0.02 AV: 1 NL: 2.08E9
T: FTMS + p ESI Full ms [100.0000-400.0000]



FS 030 #1 RT: 0.02 AV: 1 NL: 2.08E9
T: FTMS + p ESI Full ms [100.0000-400.0000]

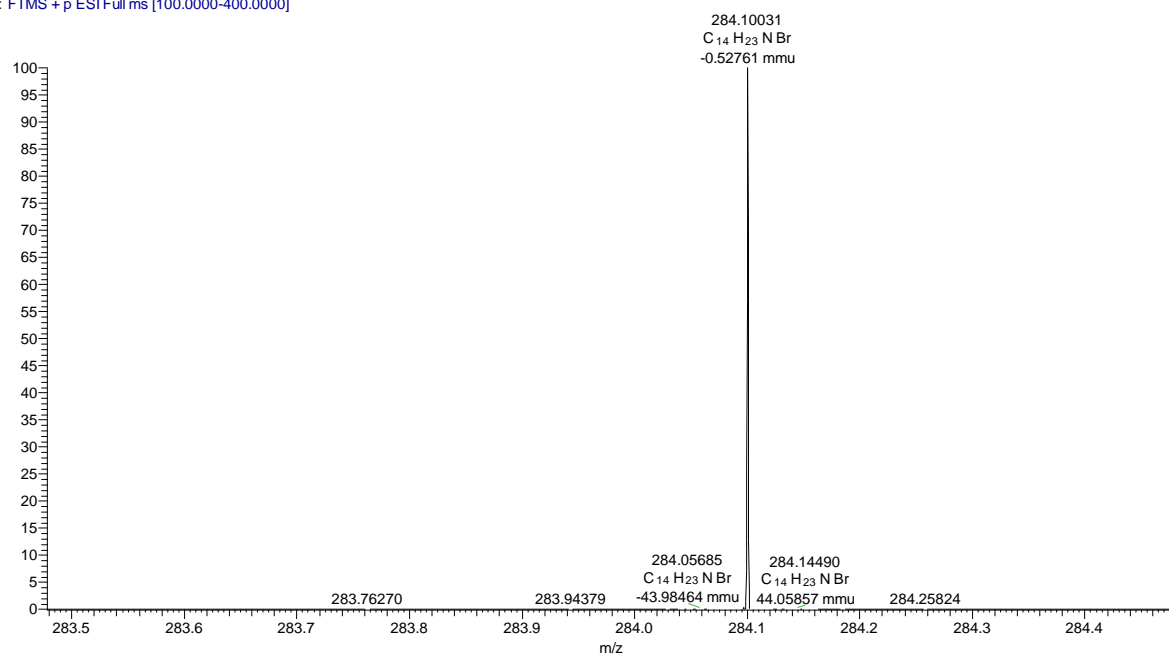


Figure S88: HR-ESI-MS of 19.

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