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Supporting Information

Challenges in the Direct Detection of Chirality-induced Spin Selectivity: Investigation of Foldamer-based Donor-acceptor Dyads

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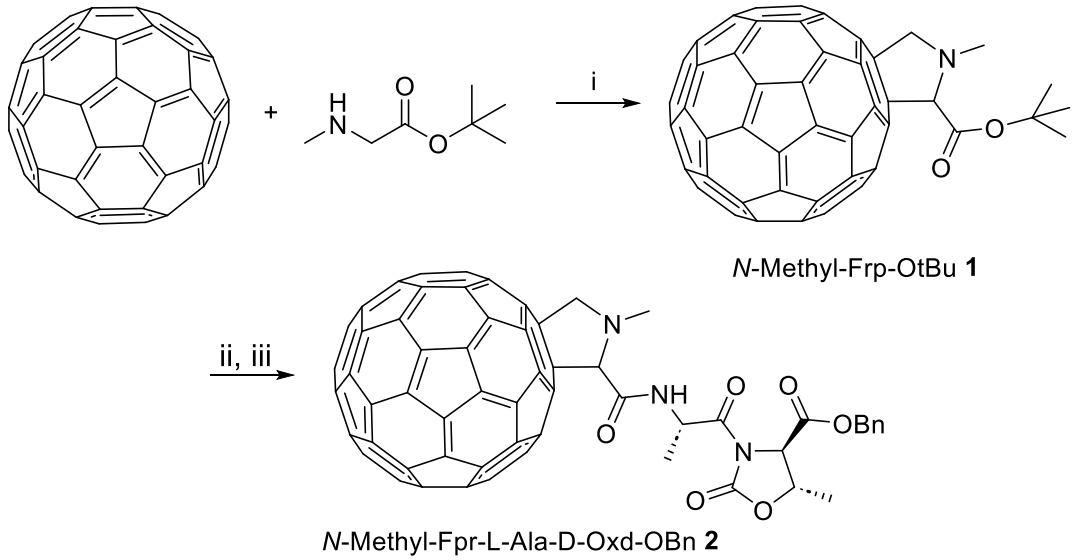
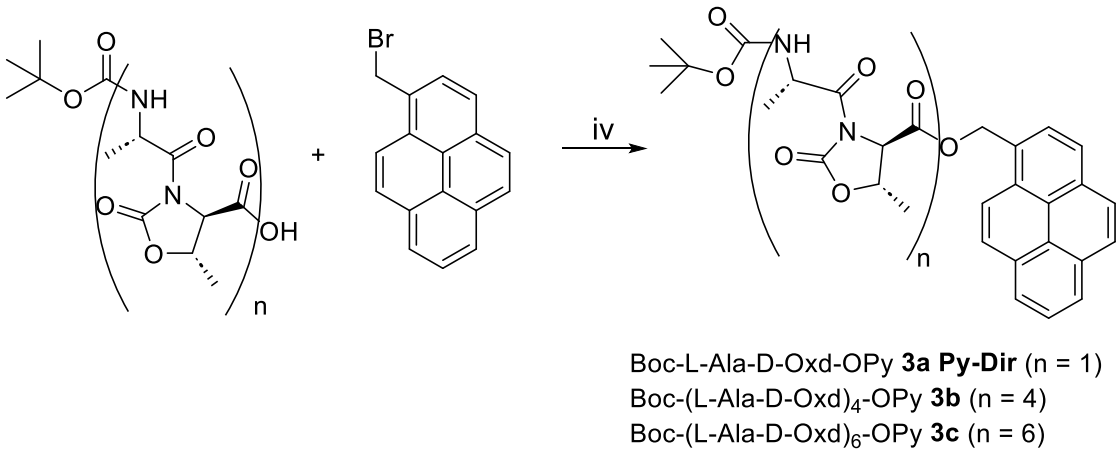
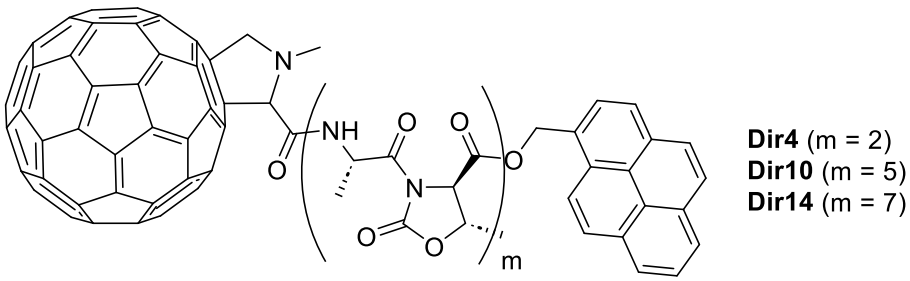
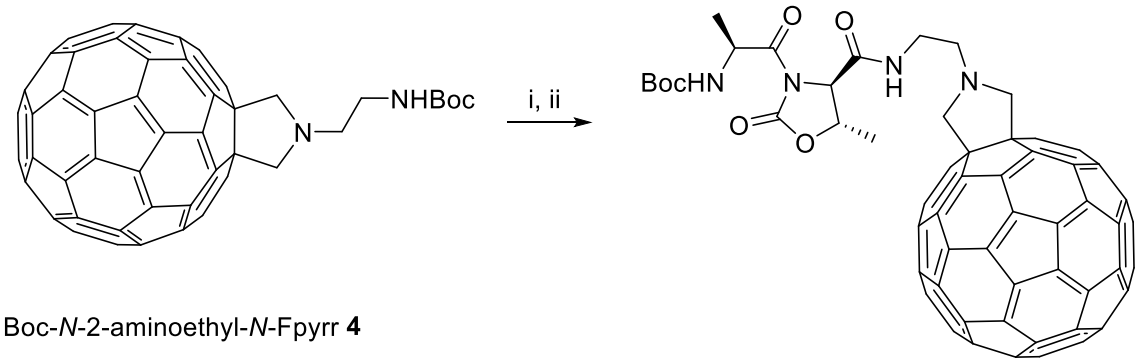
Synthetic schemes for the preparation of Dir4, Dir10, Dir14, Inv4, Inv10 and Inv14







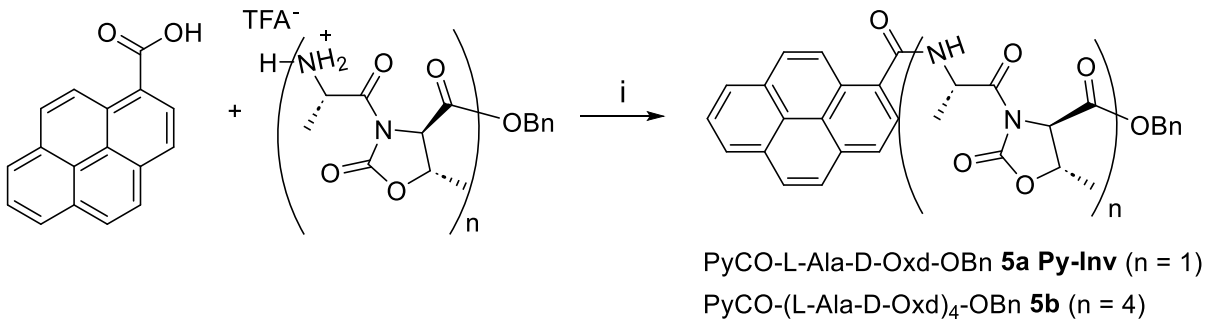
Scheme S1. Reagents and Conditions: (i) paraformaldehyde, DIEA, toluene, 1h, reflux; (ii) TFA, dry CH_2Cl_2, 4h, r.t.; (iii) TFA.H_2N-L-Ala-D-Oxd-OBn, HBTU, DIEA, dry CH_2Cl_2, 6h, r.t.; (iv) K_2CO_3, TBAB, NaI, dry ACN, 18 h, r.t.; (v) Pd/C, H_2, MeOH, 8h, r.t.; (vi) TFA, dry CH_2Cl_2, 4h, r.t.; (vii) HBTU, DIEA, dry CH_2Cl_2, 24 h, r.t.



Boc-*N*-2-aminoethyl-*N*-Fpyrr **4**

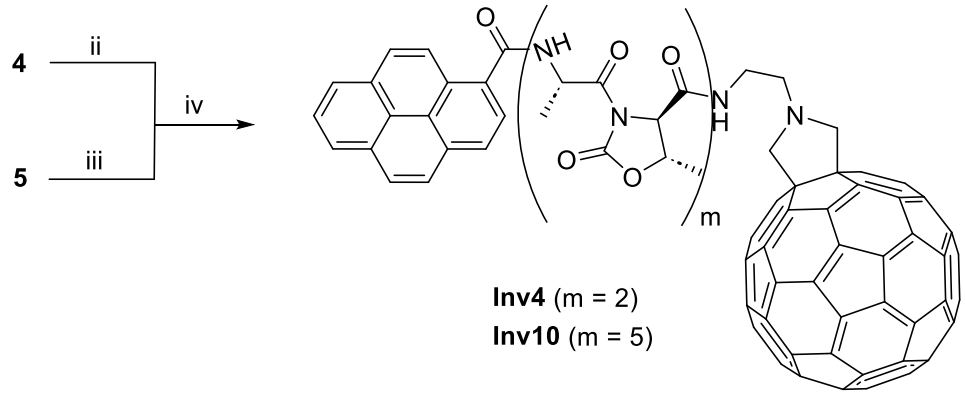
Boc-L-Ala-D-Oxd-*N*-2-aminoethyl-*N*-Fpyrr **4**

Scheme S2. Reagents and Conditions: (i) TFA, dry CH_2Cl_2, 5h, r.t.; (ii) TFA·H_2N-L-Ala-D-Oxd-OBn, HBTU, DIEA, dry CH_2Cl_2, 20h, r.t..



PyCO-L-Ala-D-Oxd-OBn **5a Py-Inv** (n = 1)

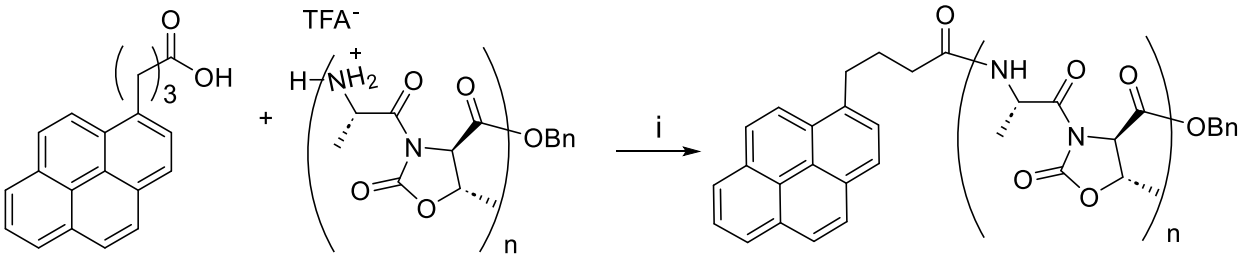
PyCO-(L-Ala-D-Oxd)$_4$-OBn **5b** (n = 4)



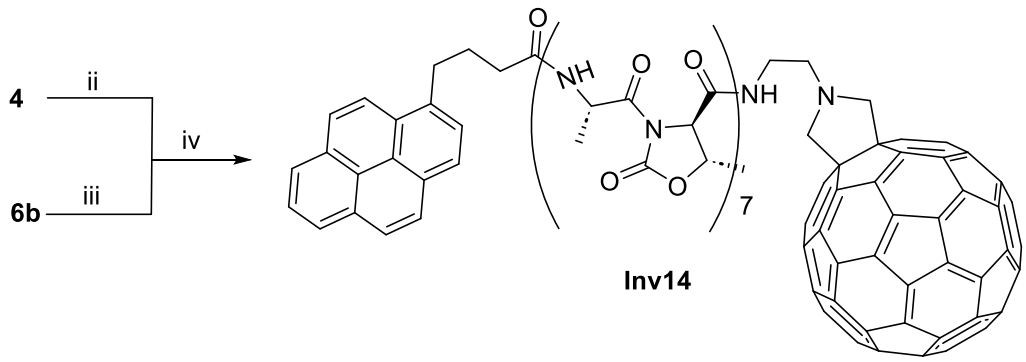
Inv4 (m = 2)

Inv10 (m = 5)

Scheme S3. Reagents and Conditions: (i) HBTU, DIEA, dry ACN, 18h, r.t.; (ii) TFA, dry CH_2Cl_2, 4h, r.t.; (iii) Pd/C, H_2, MeOH, 4h, r.t.; (vi) HBTU, DIEA, dry CH_2Cl_2, 24h, r.t.



4-Py$(CH_2)_3$CO-L-Ala-D-Oxd-OBn **6a Py-Inv'** (n=1)
4-Py$(CH_2)_3$CO-(L-Ala-D-Oxd)$_6$-OBn **6b** (n=6)



Inv14

Scheme S4. Reagents and Conditions: (i) HBTU, DIEA, dry ACN, 18h, r.t.; (ii) TFA, dry CH_2Cl_2, 4h, r.t.; (iii) Pd/C, H_2, MeOH, 4h, r.t.; (vi) HBTU, DIEA, dry CH_2Cl_2, 24h, r.t.

Preparation and Characterization of Py-Dir, Dir4, Dir10, Dir14, Py-Inv, Inv4, Inv10, Py-Inv' and Inv14

Materials - All reactions were carried out in dried glassware and using dry solvents. The melting points of the compounds were determined in open capillaries and are uncorrected. High-quality infrared spectra (64 scans) were obtained at 2 cm^{-1} resolution with an ATR-IR Bruker (Billerica, US, MA) Alpha System spectrometer. All compounds were dried in vacuo, and all the sample preparations were performed in a nitrogen atmosphere. NMR spectra were recorded with a Varian (Palo Alto, US, CA) Inova 400 spectrometer at 400 MHz (^{1}H NMR) and at 100 MHz or 151 MHz (^{13}C NMR). Unfortunately, the low solubility of these molecules in any solvent prevented the acquisition of NMR spectra with a very high signal-to-noise ratio. Chemical shifts are reported in δ values relative to the solvent peak. HPLC-MS analysis was carried out with an Agilent 1260 Infinity II liquid chromatography coupled to an electrospray ionization mass spectrometer (LC-ESI-MS), using a Phenomenex Gemini C18 - 3μ - 110 Å column, H_2O/CH_3CN with 0.2% formic acid as acid solvent at 40 °C (positive ion mode, mz = 50-2000, fragmentor 70 V). To record LC analysis of the C_{60} derivatives, the compounds were dissolved in 4/1 THF/Methanol.

The $(L\text{-}Ala\text{-}D\text{-}Oxd)_n$ derivatives were synthesized as reported in literature. The characterization matched the values reported in reference.[1]

Synthesis of (*N*-methyl)-fulleroproline *t*-butyl ester (*N*-Methyl-Fpr-O*t*Bu) 1 - Fullerene was derivatized using the same methodology reported in the literature.[2] Fullerene (250 mg, 0.347 mmol) was dissolved in toluene (150 mL). Sarcosine *t*-butyl ester hydrochloride (82 mg, 0.451 mmol) and DIEA (77 μL, 0.451 mmol) and finally paraformaldehyde (52 mg, 1.735 mmol) were added to the mixture, which was stirred under reflux for 1 h. The solvent was then dried under reduced pressure and the residue was purified with silica chromatography (95:5 toluene:EtOAc as solvent).

N-Methyl-Fpr-O*t*Bu **1** was obtained as a dark brown solid in 50% yield (151 mg, 0.172 mmol). IR (ATR-IR): ν 2976, 2915, 2840, 2775, 1777, 1736, 1662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.5 (m, 9H, tBu), 3.0 (s, 3H, NCH_3), 4.25 (d, 1H, CH CH_2N), 4.73 (s, 1H, CH α), 5.0 (d, 1H, CH CH_2N).

Synthesis of *N*-Methyl-Fpr-L-Ala-D-Oxd-OBn 2 – *N*-Methyl-Fpr-O*t*Bu **1** (150 mg, 0.171 mmol) was deprotected at the *C*-terminus by reaction with trifluoroacetic acid (TFA) (2.64 mL, 34.2 mmol) in CH_2Cl_2. After 4 hours, the excess TFA was neutralized using NaOH 1M. The organic product was extracted from the aqueous phase with CH_2Cl_2 obtaining *N*-methyl-Fpr-OH with a 84% yield.

The *N*-methyl-Fpr-OH (118 mg, 0.144 mmol) was dissolved in dry CH_2Cl_2 (3 mL) with HBTU (2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) (60 mg, 0.158 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing TFA·NH_2-L-Ala-D-Oxd-OBn (75 mg, 0.245 mmol) and DIEA (*N*,*N*-diisopropylethylamine) (55 μL, 0.316 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise to the mixture, and the reaction was stirred for 6 h at RT. The solvent was removed under reduced pressure, and the mixture was dissolved in CH_2Cl_2 and washed with H_2O, aqueous 1 M HCl, saturated solution of $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4 and the solvent evaporated under vacuum. The crude residue was purified with silica chromatography (99:1 CH_2Cl_2:MeOH as solvent). *N*-Methyl-Fpr-L-Ala-D-Oxd-OBn **2** was obtained as a brown solid in 60% yield (98 mg, 0.086 mmol). IR (ATR-IR): ν 3372, 2919, 2846, 2784, 1792, 1733, 1706, 1676 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.25 (d, 3H, CH_3 Oxd), 1.54 (d, 3H, CH_3 Ala), 2.89 (s, 3H, CH_3N), 4.22 (d, 1H, CH CH_2N), 4.50 (d, 1H, CH α Oxd), 4.56 (s, 1H, CH α Fpr), 4.61 (m, 1H, CH α-Ala), 4.88 (d, 1H, CH CH_2N), 5.28 (2H, CH_2OBn), 5.90 (m, CH β Oxd), 8.04 (d, 1H, NH).

General Method for the Preparation of 3a(Py-Dir)/3b/3c - Compounds **3a/3b/3c** were synthesised starting from the corresponding Boc-(L-Ala-D-Oxd)$_n$-OH derivatives, where n = 1, 4, 6.

The selected peptide (0.15 mmol) was dissolved in dry ACN (4 mL). Dry K_2CO_3 (41.2 mg, 0.225 mmol), TBAB (9.7 mg, 0.03 mmol) and NaI (4.5 mg, 0.03 mmol) were added to the flask, followed

by 1-bromomethylpyrene (53.1 mg, 0.180 mmol). The reaction was then left under stirring under nitrogen atmosphere for 18 h at RT. The solvent was evaporated under reduced pressure, and the crude was dissolved in CH_2Cl_2 and washed with H_2O, aqueous 1 M HCl, saturated solution of $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4, and the solvent evaporated under vacuum. The crude residue was purified with silica chromatography (99:1 CH_2Cl_2:MeOH as solvent).

Boc-L-Ala-D-Oxd-OCH$_2$Py (Py-Dir) 3a: Yield 62% (49.3 mg, 0.093 mmol). M.p. 94 °C. IR (ATR-IR): ν 3287, 3038, 2976, 2918, 2842, 1777, 1736, 1662 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.41 (d, 6H, CH_3 Ala, CH_3 Oxd), 1.45 (m, 9H, Boc), 4.45 (d, 1H, CH α Oxd), 5.28 (m, 1H, CH α Ala), 5.41 (m, 1H, CH β Oxd), 5.94 (s, 2H, OCH_2Py), 7.98-8.26 (m, 9H, CH Py). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 173.99 173.31 169.65 167.49 132.12 131.14 130.61 129.61 128.58 128.08 127.29 126.20 125.73 124.87 124.56 122.49 73.69 66.64 62.00 49.31 48.70 28.32 21.64 21.05 18.83

HPLC-MS (ESI): 11,06 min, [M+Na$^+$] = 553.

Boc-(L-Ala-D-Oxd)$_4$-OCH$_2$Py 3b: Yield 48% (81.0 mg, 0.072 mmol). M.p. 130 °C. IR (ATR-IR): ν 3287, 2976, 2853, 1777, 1736, 1662 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33-1.51 (m, 24H, 4 CH_3 Ala, 4 CH_3 Oxd), 1.53-1.65 (9H, Boc), 4.42-4.90 (m, 8H, 4 CH α Oxd, 4 CH α Ala), 5.17-5.74 (m, 4 CH β Oxd), 5.91-6.05 (2H, OCH_2Py), 6.48 (d, 1H, NH-Boc), 7.22 (1H, NH amide), 8.01-8.34 (m, 9H, CH Py). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.96, 171.97, 169.62, 159.64, 158.88, 138.26, 128.59, 127.88, 126.86, 126.28, 120.41, 115.84, 112.13, 108.55, 77.23, 77.02, 76.81, 76.04, 75.46, 62.91, 62.64, 61.67, 60.38, 59.08, 53.99, 52.48, 49.34, 49.14, 48.58, 48.45, 48.31, 46.09, 38.66, 36.33, 31.94, 29.71, 29.37, 28.29, 27.95, 24.00, 22.70, 21.18, 21.11, 21.07, 20.29, 19.75, 18.61, 17.63, 17.38, 16.86, 14.13, 13.61, 8.63. HPLC-MS (ESI): [M+NH_4^+] = 1143.

Boc-(L-Ala-D-Oxd)$_6$-OCH$_2$Py 3c: Yield 45% (102.0 mg, 0.067 mmol). M.p. 142°C. IR (ATR-IR): ν 3372, 2929, 2846, 2784, 1792, 1733, 1706, 1676 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33-1.51 (m, 45H, Boc, 6 CH_3 Ala, 6 CH_3 Oxd), 4.35-4.52 (m, 6H, CH α Oxd), 4.52-5.58 (m, 12H, 6 CH α Ala, 6 CH β Oxd), 5.73-6.04 (2H, OCH_2Py), 7.51 (1H, NH amide), 7.67 (1H, NH amide), 7.55-8.27 (m, 9H, CH Py). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.78, 175.61, 172.77, 171.32, 170.13, 168.60,

167.54, 165.85, 159.70, 159.51, 155.47, 151.83, 131.42, 131.15, 127.82, 127.34, 124.95, 124.62, 79.84, 77.29, 77.08, 76.87, 76.50, 74.96, 62.89, 62.02, 61.52, 61.17, 60.51, 58.62, 54.18, 53.26, 52.46, 49.23, 49.01, 48.76, 38.63, 31.91, 29.68, 29.34, 28.33, 23.80, 22.68, 21.10, 20.93, 20.74, 20.25, 19.62, 19.02, 18.58, 18.17, 17.57, 17.10, 14.12, 13.59. HPLC-MS (ESI): [M-Boc] = 1421.

General Method for the Preparation of Dir4/Dir10/Dir14.

Compound **2** (98 mg, 0.086 mmol) was dissolved in a mixture of MeOH (10% V/w) and CH_2Cl_2 (2% V/w) in the presence of catalytic Pd/C and a H_2 atmosphere. The reaction was left under stirring for 6 h, then the solution was filtered through a celite pad and the solvent removed under reduced pressure. The product, *N*-methyl-Fpr-L-Ala-D-Oxd-OH, was obtained as a white solid in 65% yield (58.4 mg, 0.056 mmol).

Compounds **3a**/**3b**/**3c** (0.067 mmol) were deprotected from the Boc group in quantitative yield, using TFA (0.13 mL, 1.675 mmol) in dry CH_2Cl_2 (4 mL).[1]

The previously obtained *N*-methyl-Fpr-L-Ala-D-Oxd-OH (58 mg, 0.056 mmol) was dissolved in dry CH_2Cl_2 (2 mL) with HBTU (23 mg, 0.61 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing $TFA{\cdot}NH_2$-(L-Ala-D-Oxd)$_n$-OCH_2Py (n = 1, 4, 6) (0.067 mmol) and DIEA (80 μL, 0.47 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to the mixture under nitrogen, and the reaction was stirred for 24 h at RT. The solvent was removed under reduced pressure, and the mixture was dissolved in CH_2Cl_2 and washed with brine, HCl (1 M), $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, and the solvent evaporated under vacuum.

The crude residue of **Dir4** and **Dir10** were purified with silica chromatography (99:1 CH_2Cl_2:MeOH as solvent). Pure **Dir14** was obtained washing the crude with *n*-hexane and Et_2O.

Dir4: Yield: 43% (35.0 mg, 0.024 mmol); IR (ATR-IR): ν 3366, 2922, 2851, 2789, 1789, 1736, 1702, 1672 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.35-1.50 (12H, CH_3 Ala, CH_3 Oxd), 3.01 (s, 3H, FprNCH_3), 3.65 (2H, CH α Ala), 4.05 (2H, CH α Oxd), 4.21 (d, 1H, CH_2N Fpr), 4.68 (H, CH α Fpr), 4.94 (d, 1H, CH_2N Fpr), 5.20 (1H, CH β Oxd), 5.32 (1H, CH β Oxd), 6.21 (2H, OCH_2Py), 7.80-8.45

(9H, CH Py). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.25 173.94 173.27 172.37 167.56 167.37 156.82 142.05 140.23 137.75 135.52 134.76 128.81 128.73 128.36 123.58 121.68 120.43 120.19 113.36 109.37 73.70 68.17 68.02 61.89 47.67 31.90 29.65 28.29 22.66 22.17 21.22 18.65.

Dir10: Yield: 38% (42.0 mg, 0.021 mmol); IR (ATR-IR): ν 3287, 2922, 2847, 1777, 1736, 1662 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33-1.66 (30 H, 5 CH_3 Ala, 5 CH_3 Oxd), 3.10 (s, 3H, FprNCH_3), 3.1-3.17 (5 H, CH α Ala) 3.88-4.01 (2H, CH α Oxd), 4.62 (CH β Oxd), 4.72 (2H, CH β Oxd), 5.89 (2H, OCH_2Py), 7.75-8.26 (9H, CH Py). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.58 173.46 173.29 172.44 169.97 169.39 169.12 169.02 168.65 168.61 168.50 167.95 162.23 157.84 151.13 147.40 146.20 146.05 145.95 145.39 145.31 145.27 144.53 143.20 143.06 142.61 142.22 142.04 141.85 140.49 140.13 134.54 133.99 133.88 128.88 128.79 128.49 128.31 127.90 120.30 75.62 74.88 74.03 67.90 61.84 61.78 60.29 60.19 58.65 54.14 53.34 53.01 48.82 48.24 38.59 33.57 31.89 29.66 29.43 29.33 29.23 29.07 23.75 22.66 21.09 19.58.

Dir14: Yield: 68% (93.0 mg, 0.038 mmol); IR (ATR-IR): ν 3280, 2916, 2850, 2777, 1782, 1707, 1659 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.30-1.54 (42H, 7 CH_3 Ala, 7 CH_3 Oxd) 3.00 (s, 3H, FprNCH_3), 3.16 (7 H, CH α Ala), 4.23 (d, 1H, CH_2N Fpr), 4.35-4.67 (7H, CH α Oxd), 4.70 (1H, CH α Fpr), 4.97 (d, 1H, CH_2N Fpr), 5.00-5.75 (7H, CH β Oxd) 5.83 (2H, CH_2OPy), 7.94-8.50 (9H, CH Py). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.69 185.82 176.37 168.28 167.30 164.32 161.26 159.01 157.97 155.40 154.03 153.23 151.75 151.05 147.38 147.27 146.93 146.61 146.37 146.30 146.22 146.05 145.86 145.78 145.59 145.51 145.27 144.50 144.46 144.37 143.11 143.06 142.68 142.09 141.91 141.86 140.29 140.22 139.68 139.21 137.75 136.59 135.49 131.72 131.11 130.90 130.66 130.03 124.98 119.46 118.66 117.83 117.53 113.18 109.99 83.26 79.60 74.98 73.25 72.46 69.66 68.48 65.02 61.00 58.73 56.94 55.79 52.67 51.08 48.96 47.61 47.41 45.45 39.80 31.90 29.63 29.33 28.28 25.92 23.79 22.66 20.75 19.61 17.96 17.85 14.09 13.52.

Synthesis of Boc-L-Ala-D-Oxd-*N*-2-aminoethyl-*N*-fulleropyrrolidine 4 - Boc-*N*-aminoethyl-N-fulleropyrrolidine (Boc-*N*-aminoethyl-N-Fpyrr) (136 mg, 0.150 mmol) was dissolved in dry CH_2Cl_2

(5 mL) with TFA (2.32 mL, 30 mmol). The mixture was stirred for 5 h at room temperature then the solvent was removed under reduced pressure. The product was obtained in quantitative yield and used for the following reaction without any purification.

Boc-L-Ala-D-Oxd-OH (71 mg, 0.225 mmol) was dissolved in dry CH_2Cl_2 (3 mL) with HBTU (114 mg, 0.300 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing $TFA{\cdot}NH_2$-$(CH_2)_2$-Fpyrr (122 mg, 0.150 mmol) and DIEA (150 μL, 0.88 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to the mixture, and the reaction was stirred for 20 h at RT. The solvent was removed under reduced pressure, and the residue was purified with silica chromatography (99:1 CH_2Cl_2:MeOH as solvent). Compound **7** was obtained as a brown solid with a yield of 53% (88 mg, 0.08 mmol). IR (ATR-IR): ν 3372, 2919, 2846, 2784, 1792, 1676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.31-1.44 (6H, CH_3 Ala, CH_3 Oxd), 1.46-1.5 (9H, Boc), 3.26 (t, 2H, CH_2N pyrrolidine), 3.52 (t, 2H, C*H*$_2$$CH_2N$ pyrrolidine), 4.45 (4H, CH_2 pyrrolidine), 4.57 (d, 1H, CH α Oxd), 4.95 (m, 1H, CH α Ala), 5.07 (1H, NH Boc), 5.29 (m, 1H, CH β Oxd).

General Method for the Preparation of 5a(Py-Inv)/5b – 1-Pyrencarboxylic acid (120 mg, 0.490 mmol) was dissolved in dry ACN (4 mL) with HBTU (204 mg, 0.539 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing $TFA{\cdot}NH_2$-$(L\text{-}Ala\text{-}D\text{-}Oxd)_n$-OBn (n=1, 4) (0.490 mmol) and DIEA (250 μL, 1.47 mmol) in dry ACN (3 mL) was added dropwise to the mixture, and the reaction was stirred for 18 h at RT. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with H_2O, aqueous 1M HCl, saturated solution of $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified with silica chromatography (99:1 CH_2Cl_2:MeOH as solvent). The products are obtained as light-yellow solids.

PyCO-L-Ala-D-Oxd-OBn (Py-Inv) 5a: Yield 82% (214 mg, 0.402 mmol). M.p. 115°C. IR (ATR-IR): ν 3287, 3038, 2976, 2918, 2850, 2775, 2327, 1777, 1662 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.55 (d, 3H, CH_3 Oxd), 1.67 (d, 3 H, CH_3 Ala), 4.53 (d, 1H, CH α Oxd), 4.62 (m, 1H, CH α Ala),

5.23 (m, 2H, CH_2 Bn), 6.04 (m, 1H, CH β Oxd), 6.90 (d, 1H, NH), 7.30 (m, 5H, CH Ph), 7.98-8.64 (m, 9H, CH Py). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.55 169.00 167.48 151.27 134.61 132.64 131.09 130.65 130.13 128.85 128.72 128.40 127.07 126.27 125.72 124.77 124.50 124.21 73.97 68.14 62.11 49.03 21.79 21.18 18.65. HPLC-MS (ESI): 9,85 min, $[M+H^+]$ = 535.

PyCO-(L-Ala-D-Oxd)$_4$-OBn 5b: Yield 73% (404 mg, 0.358 mmol). M.p. 131°C. IR (ATR-IR): ν 3280, 2916, 2850, 2777, 1782, 1707, 1659 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.98-1.50 (24 H, CH_3 Oxd, CH_3 Ala), 4.07-4.42 (d, 4H, CH α Oxd), 4.42-4.73 (m, 4H, CH α Ala), 4.80-5.27 (m, 4H, CH β Oxd), 5.80 (2H, CH_2 Bn), 6.31 (1H, NH), 7.07 (1H, NH), 7.15-7.38 (m, 5H, CH Ph), 7.60-8.34 (m, 9H, CH Py), 8.49 (1H, NH). HPLC-MS (ESI): 9.48 min, $[M+H_3O^+]$ = 1148. ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.07, 172.64, 171.87, 171.41, 171.01, 170.31, 169.77, 169.47, 169.06, 168.70, 168.15, 167.63, 167.45, 167.20, 166.35, 165.47, 158.82, 157.86, 152.54, 152.32, 151.60, 151.50, 151.29, 151.17, 151.03, 135.04, 134.60, 134.42, 131.58, 131.28, 130.97, 130.42, 129.94, 129.57, 129.24, 128.96, 128.88, 128.80, 128.78, 128.75, 128.73, 128.48, 128.45, 128.40, 128.37, 128.26, 128.11, 127.87, 127.39, 127.18, 127.04, 126.72, 126.43, 126.21, 126.13, 125.95, 125.70, 125.39, 125.08, 124.79, 124.26, 124.06, 123.85, 123.47, 123.13, 120.35, 77.28, 77.07, 76.86, 75.56, 75.32, 75.04, 74.79, 74.13, 73.95, 73.81, 68.59, 68.11, 67.87, 67.60, 62.96, 62.27, 62.08, 61.97, 61.79, 61.69, 60.92, 60.32, 52.43, 49.76, 49.42, 48.80, 48.46, 48.25, 38.66, 31.94, 29.71, 29.37, 22.70, 22.50, 21.08, 21.04, 20.91, 20.74, 20.63, 20.57, 20.27, 19.40, 18.96, 18.72, 18.55, 18.32, 18.12, 17.92, 16.11, 14.14.

Synthesis of Inv4 and Inv10 - The two compounds PyCO-L-Ala-D-Oxd-OBn **5a** and PyCO-(L-Ala-D-Oxd)$_4$-OBn **5b** were then deprotected from the benzyl group by hydrogenolysis.

PyCO-(L-Ala-D-Oxd)$_n$-OBn (0.085mmol) was dissolved in MeOH in presence of catalytic Pd/C and a H_2 atmosphere. The reaction was left under stirring for 6 h, then the solution was filtered through a celite pad, and the solvent removed under reduced pressure. PyCO-(L-Ala-D-Oxd)$_n$-OH was obtained in quantitative yield and used without further purification in the following reaction.

5a: from 45.5 mg of PyCO-L-Ala-D-Oxd-OBn in 5 mL of MeOH, with 5 mg of Pd/C we obtained 37.7 mg of PyCO-L-Ala-D-Oxd-OH;

5b: from 96 mg of PyCO-(L-Ala-D-Oxd)$_n$-OBn in 10 mL of MeOH, with 10 mg of Pd/C we obtained 88.2 mg of PyCO-(L-Ala-D-Oxd)$_4$-OH.

Boc-L-Ala-D-Oxd-*N*-2-aminoethyl-*N*-Fpr **4** (85 mg, 0.077 mmol) was dissolved in dry CH_2Cl_2 (3 mL,) with TFA (0.150 μL, 1.925 mmol) and stirred for 5 h at room temperature. Then the mixture was concentrated, and the product was obtained in quantitative yield and further used without any purification.

Py-CO-(L-Ala-D-Oxd)$_n$-OH (n = 1, 4) (0.085 mmol) was dissolved in dry CH_2Cl_2 (3 mL) with HBTU (35 mg, 0.092 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing TFA·NH_2-(L-Ala-D-Oxd)-NH-$(CH_2)_2$Fpyrr (77 mg, 0.077 mmol) and DIEA (50 μL, 0.294 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to the mixture, and the reaction was stirred for 24 h at RT. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with brine, aqueous 1M HCl, saturated solution of $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified with silica chromatography (99:1 CH_2Cl_2:MeOH for product **Inv4**, 97:3 CH_2Cl_2:MeOH for product **Inv10**) and products were obtained as light brown solids.

Inv4: Yield: 34.5% (38 mg, 0.026 mmol); IR (ATR-IR): ν 2970, 2918, 2847, 2776, 1736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32-1.52 (12H, CH_3 Ala, CH_3 Oxd), 3.16 (m, 2H, CH_2Npyrrolidine), 3.24 (m, 2H, C*H*$_2$CH$_2$Npyrrolidine), 4.20-4.33 (d, 2H, CH α Oxd), 4.41 (m, 4H, CH_2 pyrrolidine), 4.54-4.72 (m, 2H, CH α Ala), 4.81-4.98 (m, 2H, CH β Oxd), 8.00-8.25 (m, 9H, CH Py). ^{13}C NMR (100 MHz, DMSO): δ 178.04 175.68 170.43 168.49 165.38 164.16 148.45 147.40 146.13 145.15 142.53 139.91 139.66 138.95 95.48 76.08 76.01 61.12 60.84 54.11 54.00 52.42 48.11 29.44 27.74 21.16 16.96.

Inv10: Yield: 27.5% (43 mg, 0.021 mmol); IR (ATR-IR): ν 3287, 2922, 2847, 2112, 1736, 1662 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35-1.53 (m, 30H, CH_3 Ala, CH_3 Oxd), 3.29 (m, 2H, CH_2N pyrrolidine), 3.55 (m, 2H, C*H*$_2$CH2N pyrrolidine), 3.81-4.07 (d, 5H, CH α Oxd), 4.28 (m, 2H, CH α Ala), 4.43 (m, 4H, CH_2 pyrrolidine), 4.52 (m, 3H, CH α Ala), 4.58-4.80 (m, 5H, CH β Oxd), 7.95-8.26 (m, 9H, CH Py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.26 177.75 173.47 172.78 172.41 170.09 169.82 169.57 169.16 169.07 168.98 168.79 168.68 168.55 168.46 168.30 168.21 168.11 167.07 166.12 165.74 158.90 148.40 147.29 146.23 146.05 145.94 145.39 145.27 144.53 143.20 143.06 142.61 142.22 142.04 141.85 140.49 140.13 137.11 136.03 130.89 128.91 127.12 126.84 125.89 124.30 74.06 70.59 67.42 61.75 55.33 52.56 50.81 48.15 43.32 38.59 31.89 29.62 22.66 21.07 19.88 18.61 17.56 17.19 14.08 12.40.

Synthesis of 4-Py$(CH_2)_3$CO-L-Ala-D-Oxd-OBn Py-Inv' (6a) - 1-Pyrenebutyric acid (100 mg, 0.347 mmol) was dissolved in dry ACN (3 mL) with HBTU (144.6 mg, 0.381 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing TFA·NH_2-L-Ala-D-Oxd-OBn (0.347 mmol) and DIEA (200 μL, 1.18 mmol) in dry ACN (3 mL) was added dropwise to the mixture, and the reaction was stirred for 18 h at RT. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with H_2O, aqueous 1M HCl, saturated solution of $NaHCO_3$and H_2O. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified with silica chromatography (99:1 CH_2Cl_2:MeOH as solvent). The product was obtained as light-yellow solid with 85% yield (170 mg, 0.295mmol). M.p. 180-183 °C (degr.). IR (ATR-IR): ν 3287, 2976, 2918, 2856, 2775, 1777, 1736, 1662 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.42 (d, 3H, CH_3 Oxd), 1.51 (d, 3 H, CH_3 Ala), 2.19 (m, 2H, CH_2 β PyBu), 2.30 (t, 2H, CH_2 α PyBu), 3.38 (dt, 2H, CH_2 γ PyBu), 4.44 (d, 1H, CH α Oxd), 4.55 (m, 1H, CH α Ala), 5.16 (2H, CH_2 Bn), 5.69 (m, 1H, CH β Oxd), 6.12 (d, 1H, NH), 7.26 (m, 5H, CH Ph), 7.81-8.31 (m, 9H, CH Py). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.60 171.10 167.35 151.04 135.91 134.54 131.42 130.93 129.94 128.73 128.33 127.43 126.68 125.82 124.99 124.76 123.46 73.79 68.07 61.97 48.14 35.79 32.70 27.28 21.15 18.69. HPLC-MS (ESI): $[m+H^+]$ = 577, $[m+Na^+]$ = 599.

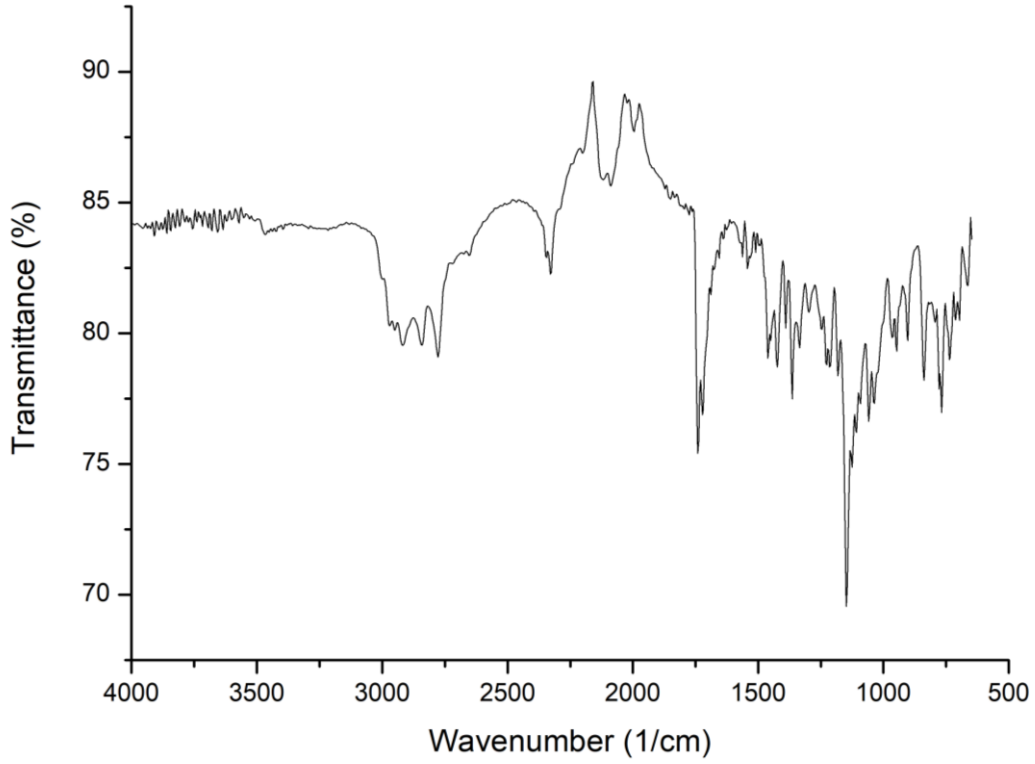
Synthesis of 4-Py(CH_2)$_3$CO-(L-Ala-D-Oxd)$_6$-OBn 6b - 1-Pyrenebutyric acid (100 mg, 0.347 mmol) was dissolved in dry ACN (3 mL) with HBTU (144.6 mg, 0.381 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing TFA·NH_2-(L-Ala-D-Oxd)$_6$-OBn (0.347 mmol) and DIEA (200 μL, 1.18 mmol) in dry ACN (3 mL) was added dropwise to the mixture, and the reaction was stirred for 24 h at RT. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with H_2O, aqueous 1M HCl, saturated solution of $NaHCO_3$and H_2O. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was washed with Et_2O and *n*-hexane. The product was obtained pure as a light-yellow solid with 92% yield (500 mg, 0.319 mmol). M.p. 182°C. IR (ATR-IR): ν 3372, 2919, 2846, 2784, 1792, 1733, 1676 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.04-1.62 (m, 45 H, 9 H Boc, 6 CH_3 Oxd, 6 CH_3 Ala), 1.93 (m, 2H, CH_2 β PyBu), 2.13 (t, 2H, CH_2 α PyBu), 3.42 (m, 2H, CH_2 γ PyBu), 4.26-4.57 (d, 6H, CH α Oxd), 4.58- 5.11 (m, 6H, CH α Ala), 5.12-5.69 (m, 6H, CH β Oxd), 5.76-5.97 (2H, CH_2 Bn), 7.24-7.41 (5H, CH Ph), 7.66-8.45 (m, 9H, CH Py). HPLC-MS (ESI): [M+Na^+] = 1590.

Synthesis of Inv14 –Py(CH_2)$_3$CO-(L-Ala-D-Oxd)$_6$-OBn (138 mg, 0.088 mmol) was dissolved in MeOH (15 mL) in presence of catalytic Pd/C (15 mg) and a H_2 atmosphere. The reaction was left under stirring for 8 h, then the solution was filtered through a celite pad, and the solvent removed under reduced pressure. Py(CH_2)$_3$CO-(L-Ala-D-Oxd)$_6$-OH was obtained in quantitative yield (130 mg, 0.088mmol) and used without further purification in the following reaction.

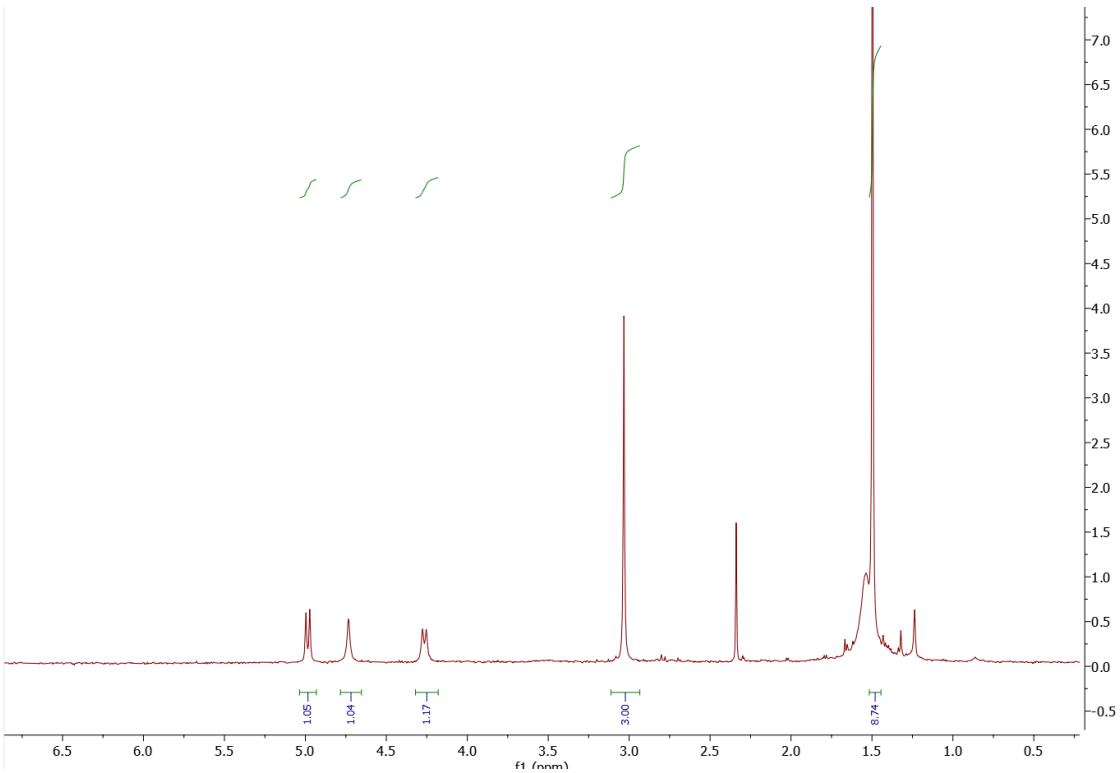
Py(CH_2)$_3$CO-(L-Ala-D-Oxd)$_6$-OH (130 mg, 0.088 mmol) was dissolved in dry CH_2Cl_2 (4 mL) with HBTU (36.4 mg, 0.096 mmol) under nitrogen atmosphere and stirred at RT for 10 minutes. A solution containing TFA·NH_2(L-Ala-D-Oxd)-NH-(CH_2)$_2$Fpyrr (80 mg, 0.088 mmol) and DIEA (80 μL, 0.470 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise to the mixture, and the reaction was stirred for 24 h at RT. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with brine, aqueous 1M HCl, saturated solution of $NaHCO_3$ and brine. The organic layer

was dried over Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was washed three times with *n*-hexane and once with MeOH. The product was obtained as a light brown solid with 45% yield (90 mg, 0.036 mmol). IR (ATR-IR): ν 3280, 2916, 2850, 2777, 1782, 1739, 1659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.29-1.64 (m, 51H, 7 CH_3 Ala, 7 CH_3 Oxd, Boc), 2.09-2.22 (m, 2H, CH_2 β PyBu), 2.23-2.34 (t,2H, CH_2 α PyBu), 3.27-3.39 (m, 2H, CH_2 γ PyBu), 3.68 (t, 2H, CH_2N pyrrolidine), 3.72 (t, 2H, C*H*$_2$CH2N pyrrolidine), 3.88-4.53 (m, 11H, 7 CH α Oxd, 2 CH_2 pyrrolidine), 4.53-5.71 (m, 14H, 7 CH α Ala, 7 CH β Oxd), 5.85 (2H, O*CH*$_2$Py), 7.80-8.18 (m, 9H, CH Py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.35 171.40 171.28 171.13 168.73 168.58 152.23 151.72 147.23 146.20 145.98 145.91 145.19 144.43 142.54 142.47 141.95 141.78 131.58 131.37 130.87 128.78 128.72 128.68 128.47 128.31 128.22 127.44 125.87 124.94 124.83 124.58 123.27 109.99 74.92 67.87 62.84 61.98 60.37 49.07 48.68 48.58 48.40 38.58 35.61 35.00 32.79 31.89 29.67 29.63 29.33 27.02 23.85 22.66 20.95 20.80 19.20 19.10 18.44 18.06 14.17.

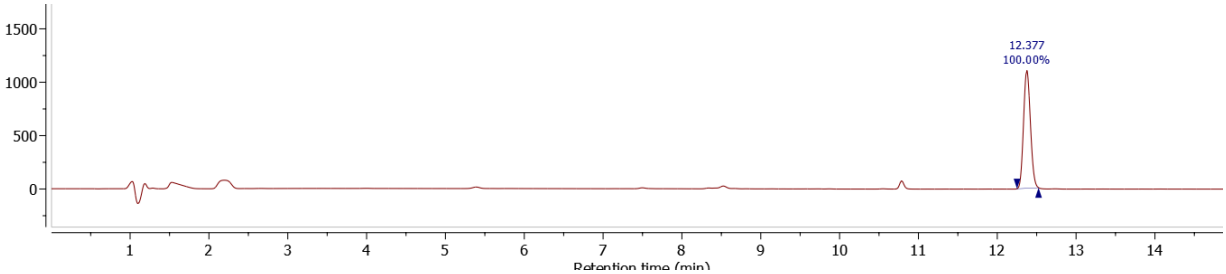
ATR-IR spectrum of ***N*-Methyl-Fpr-O*t*Bu 1**



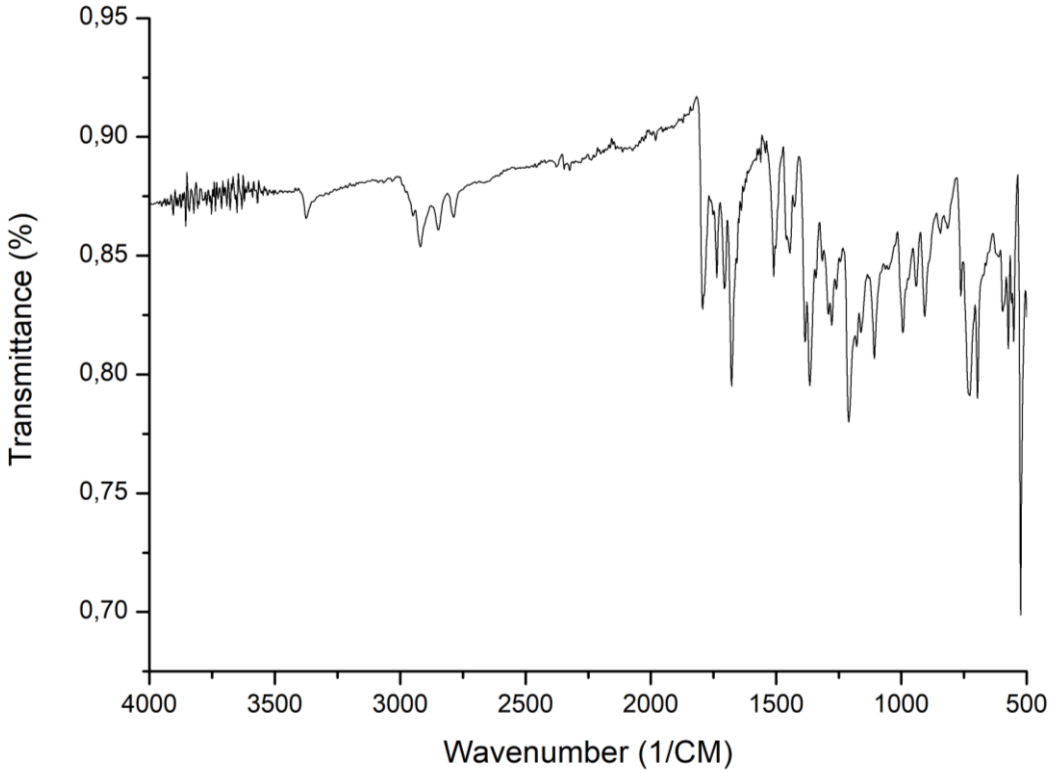
^{1}H NMR spectrum of ***N*-Methyl-Fpr-O*t*Bu 1**



HPLC analysis of ***N*-Methyl-Fpr-O*t*Bu 1**



ATR-IR spectrum of ***N*-Methyl-Fpr-L-Ala-D-Oxd-OBn 2**



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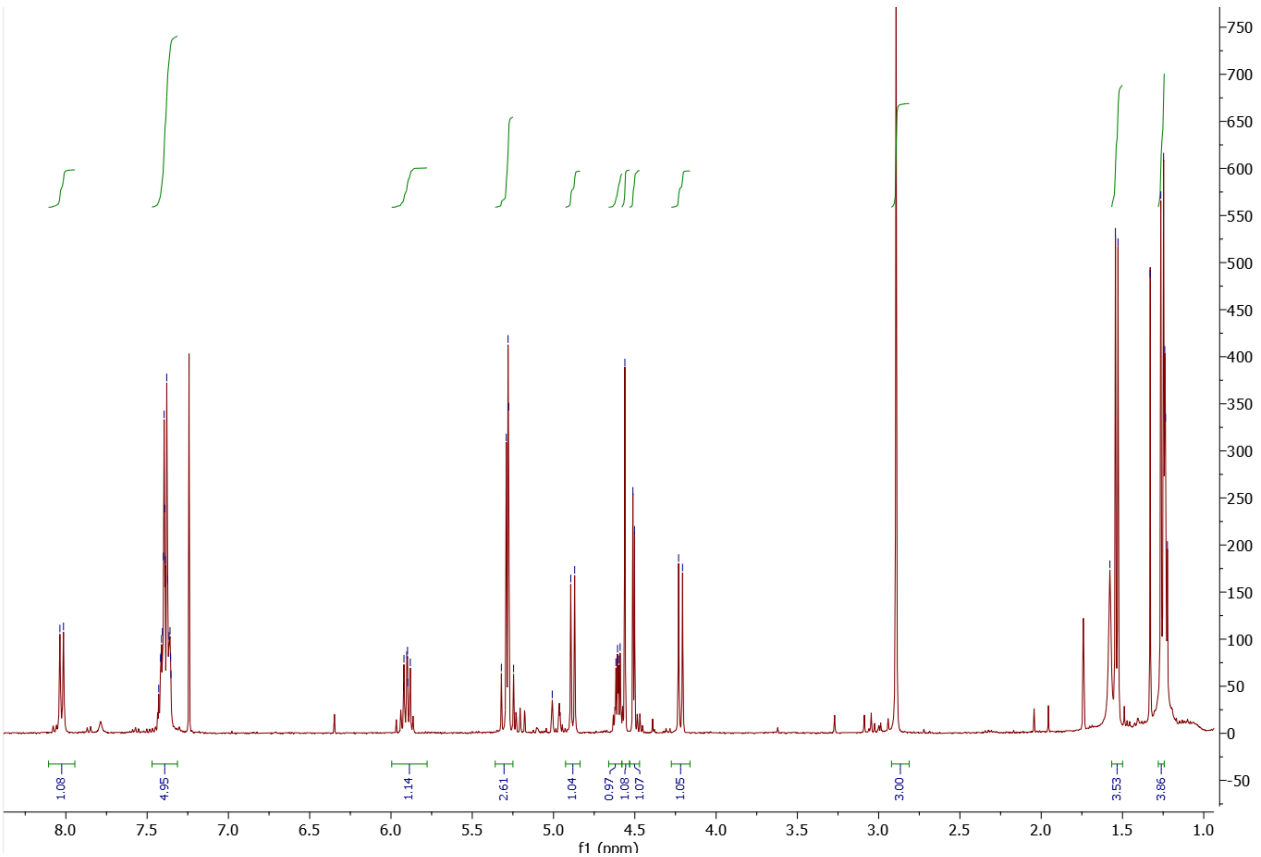
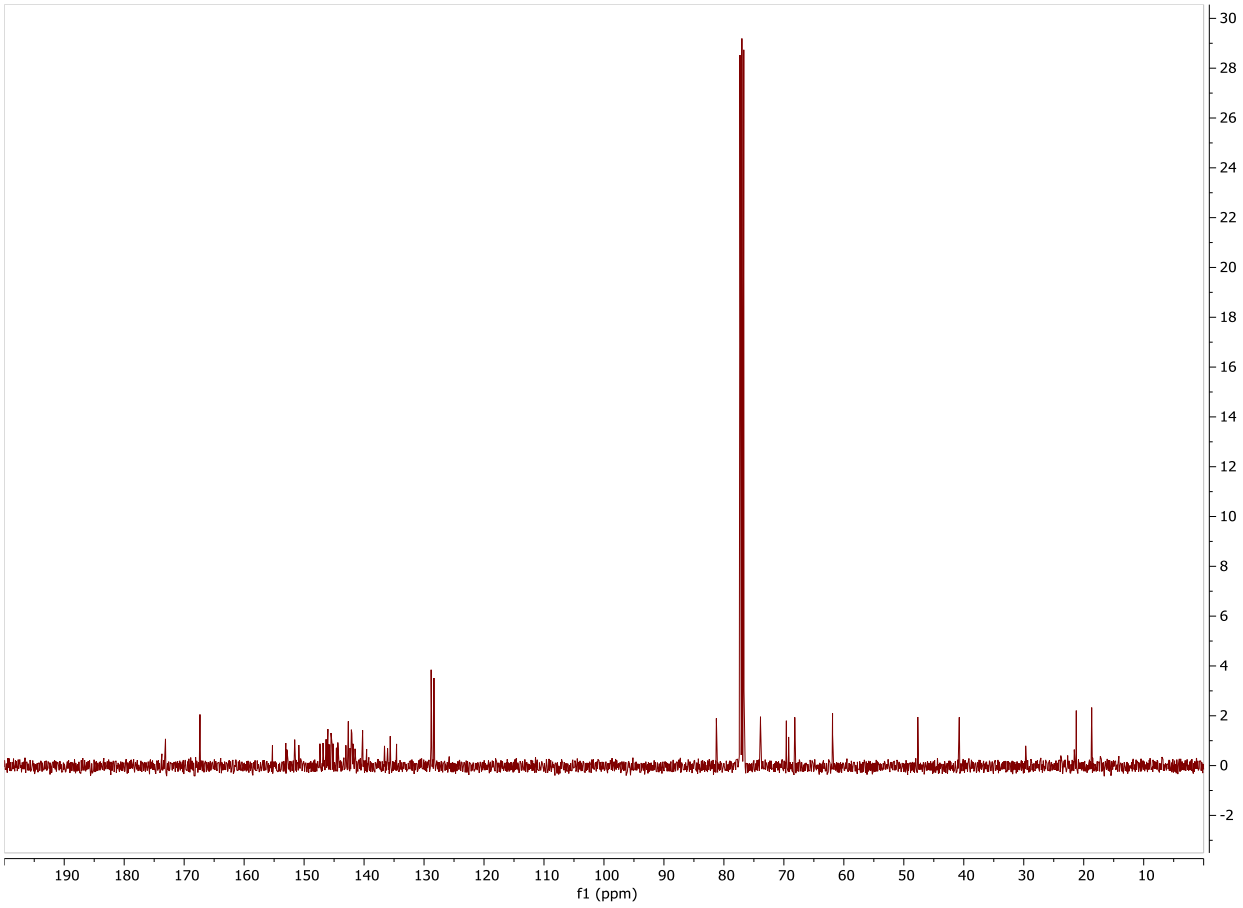
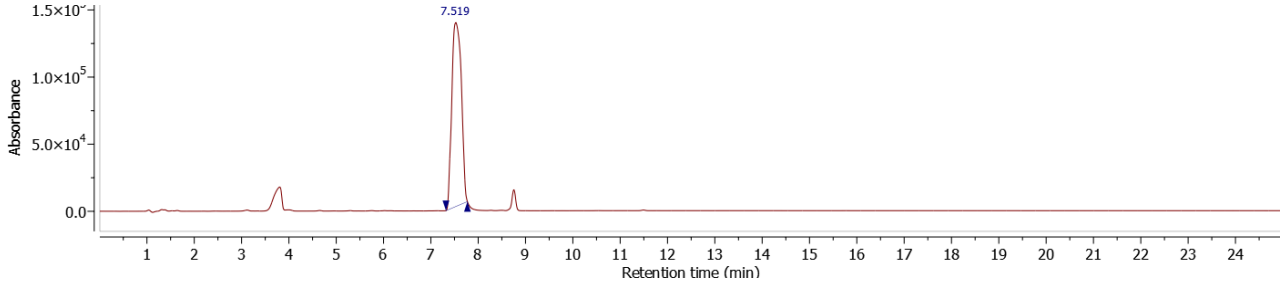


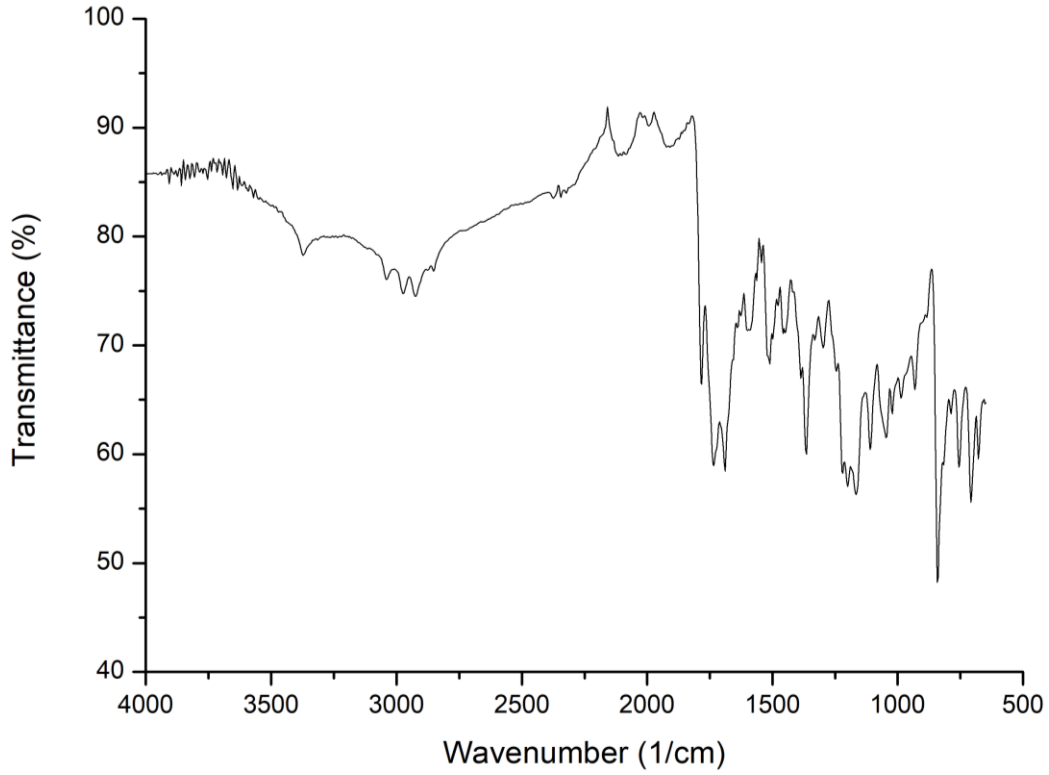
^{13}C NMR spectrum of ***N*-Methyl-Fpr-L-Ala-D-Oxd-OBn 2**



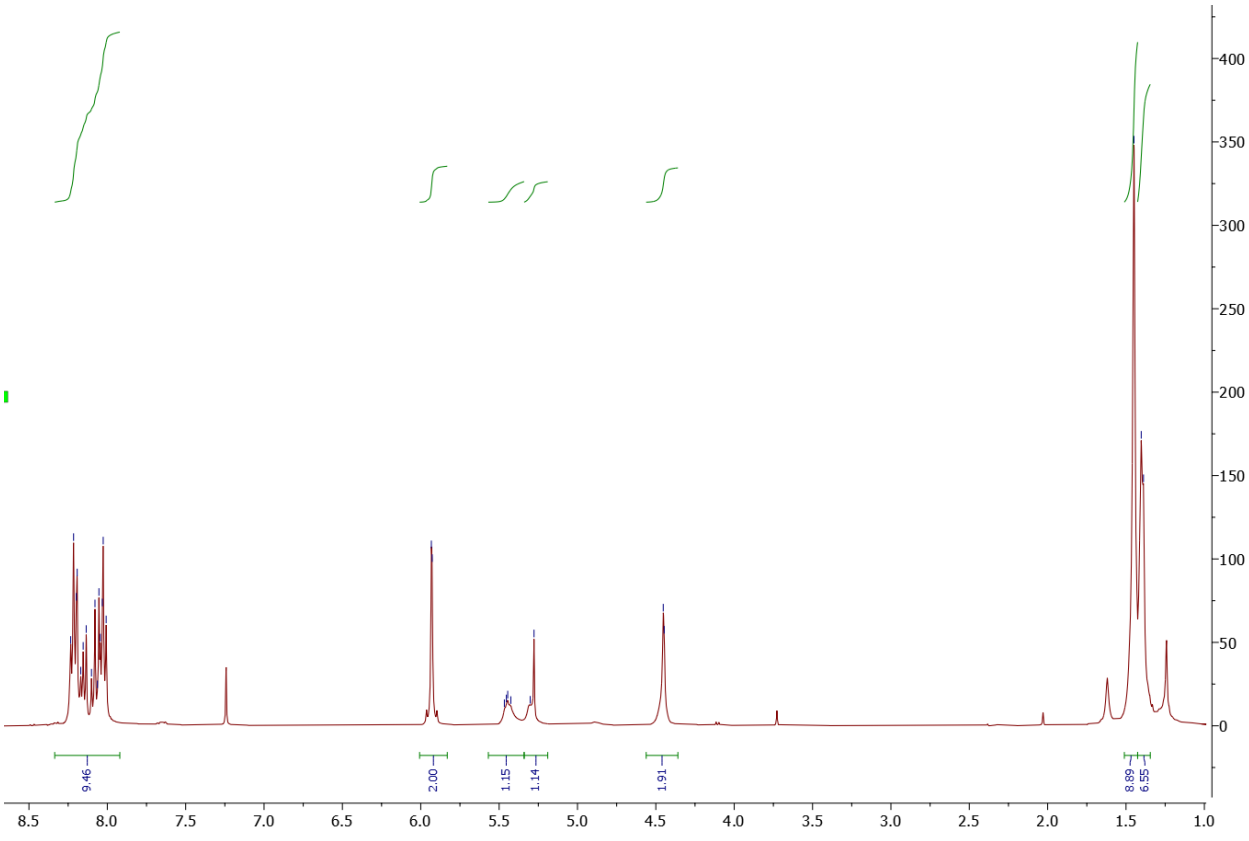
HPLC analysis of ***N*-Methyl-Fpr- L-Ala-D-Oxd-OBn 2**



ATR-IR spectrum of **Boc-L-Ala-D-Oxd-OCH$_2$Py 3a Py-Dir**



^{1}H NMR spectrum of **Boc-L-Ala-D-Oxd-OCH$_2$Py 3a Py-Dir**



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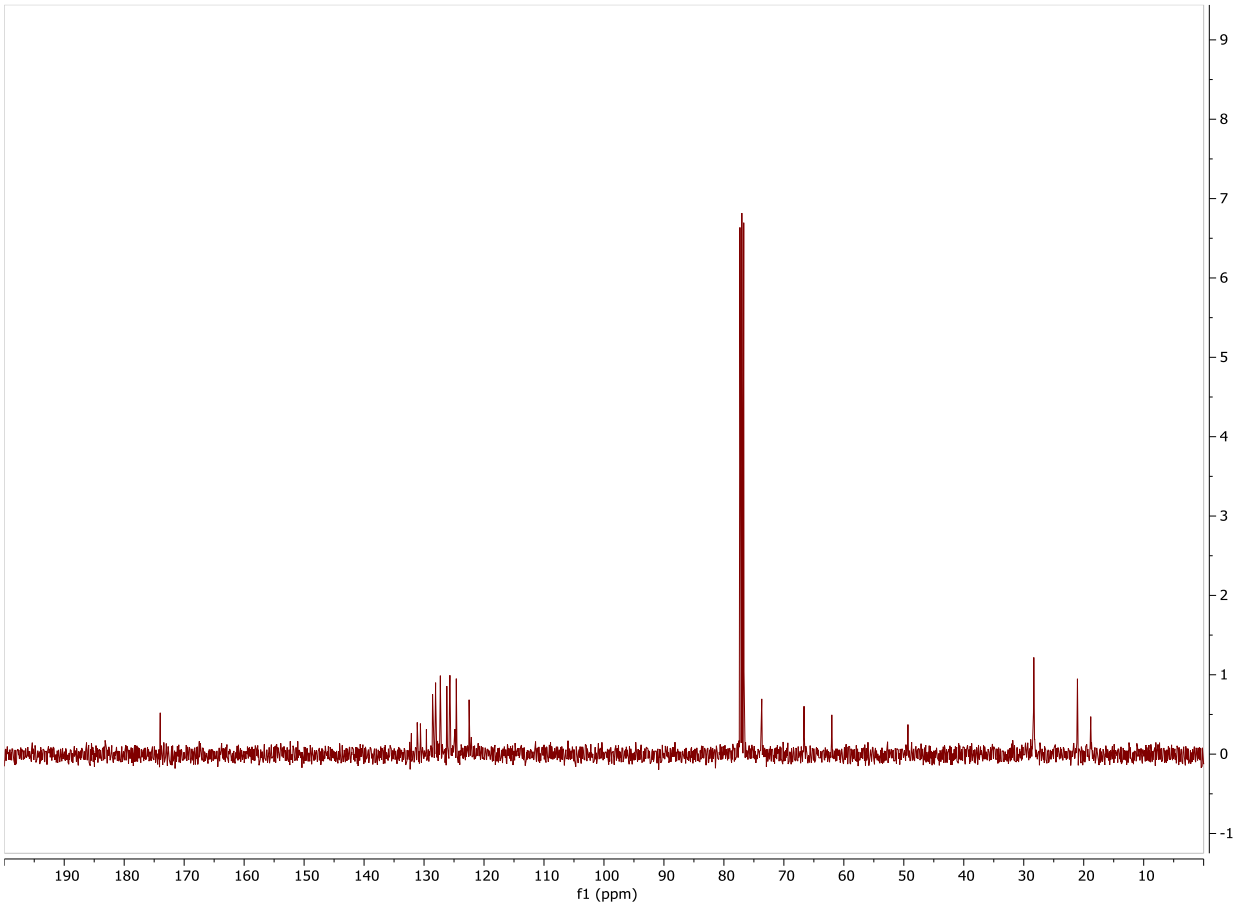
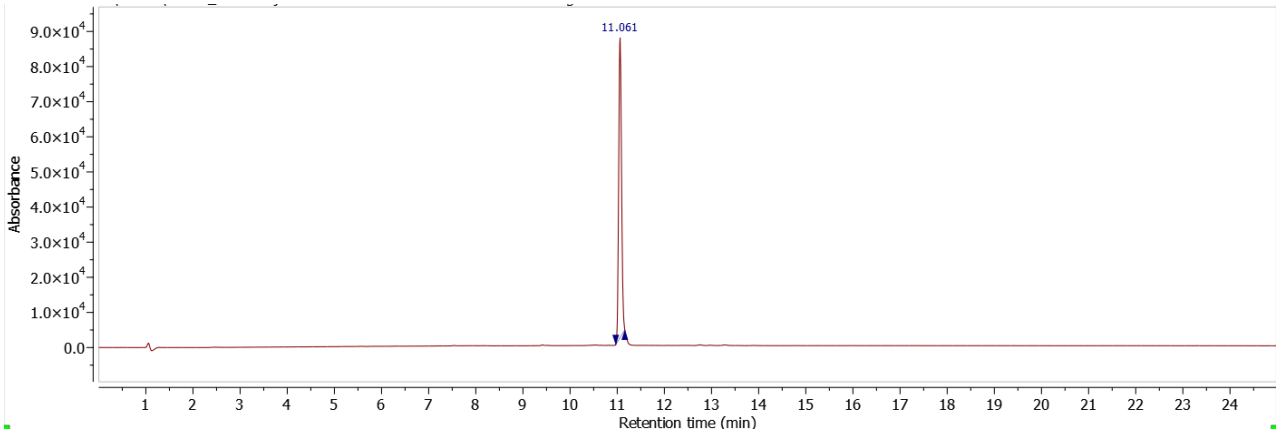
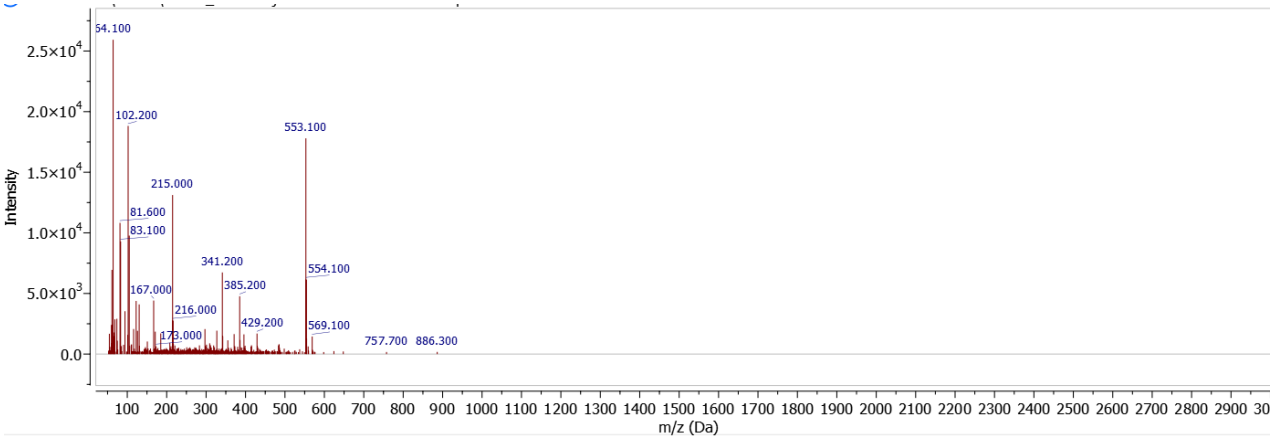
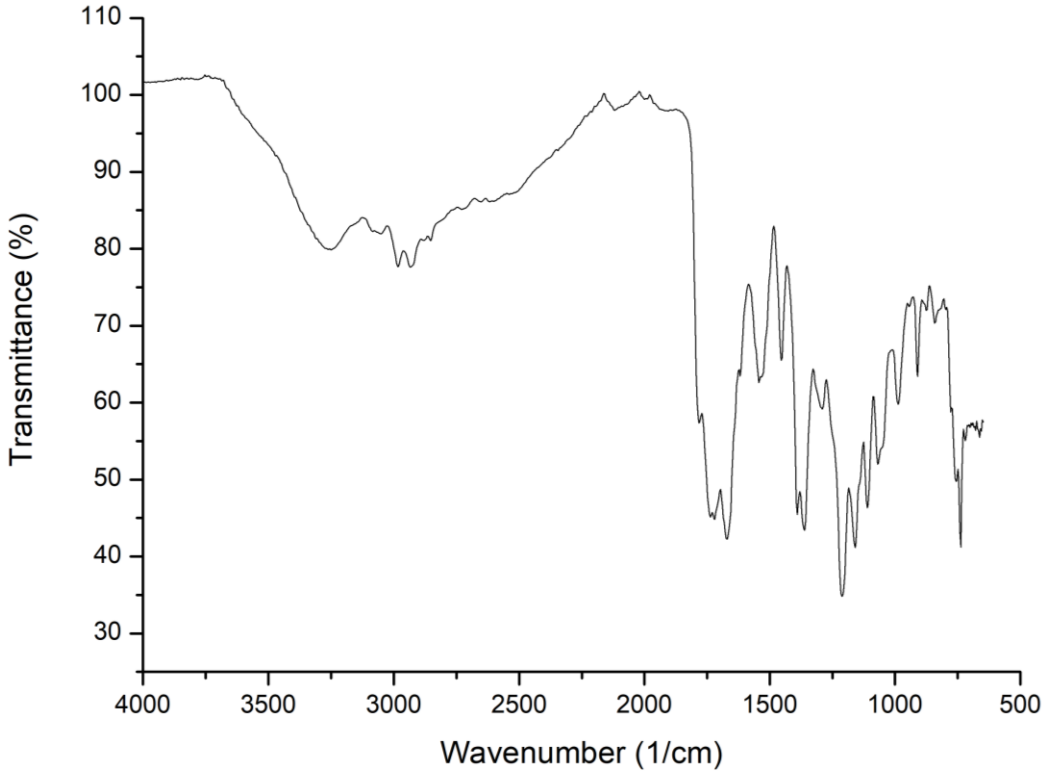


HPLC-MS analysis of **Boc-L-Ala-D-Oxd-OCH$_2$Py 3a Py-Dir**

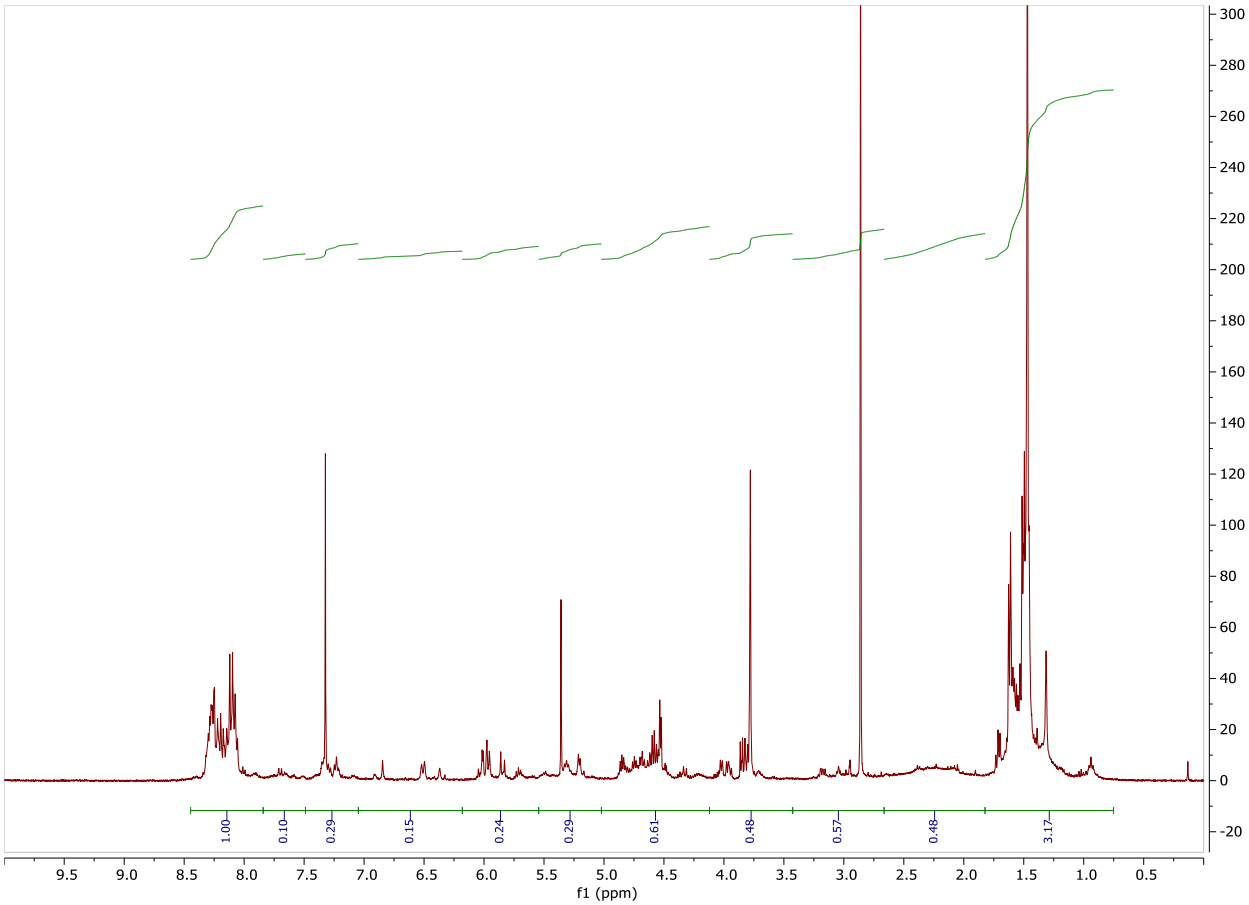




ATR-IR spectrum of **Boc-(L-Ala-D-Oxd)$_4$-OCH$_2$Py 3b**



^{1}H NMR spectrum of **Boc-(L-Ala-D-Oxd)$_4$-OCH$_2$Py 3b**



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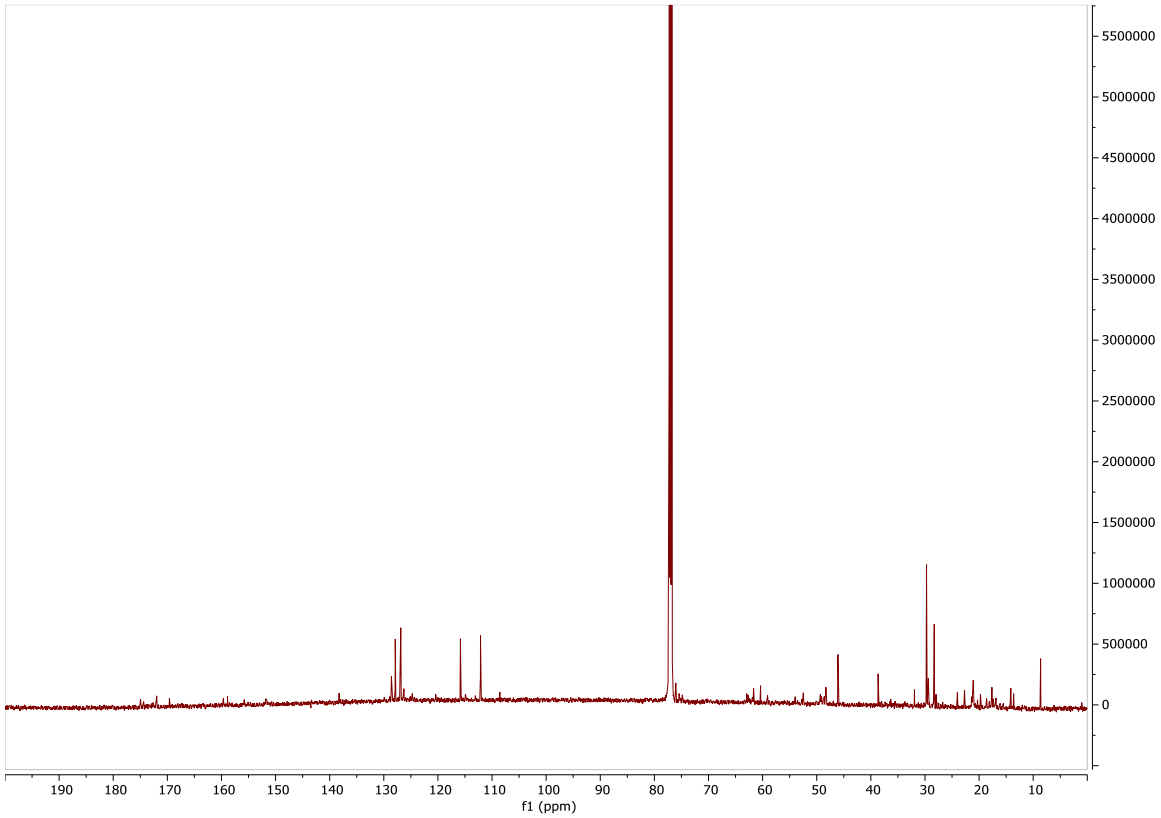
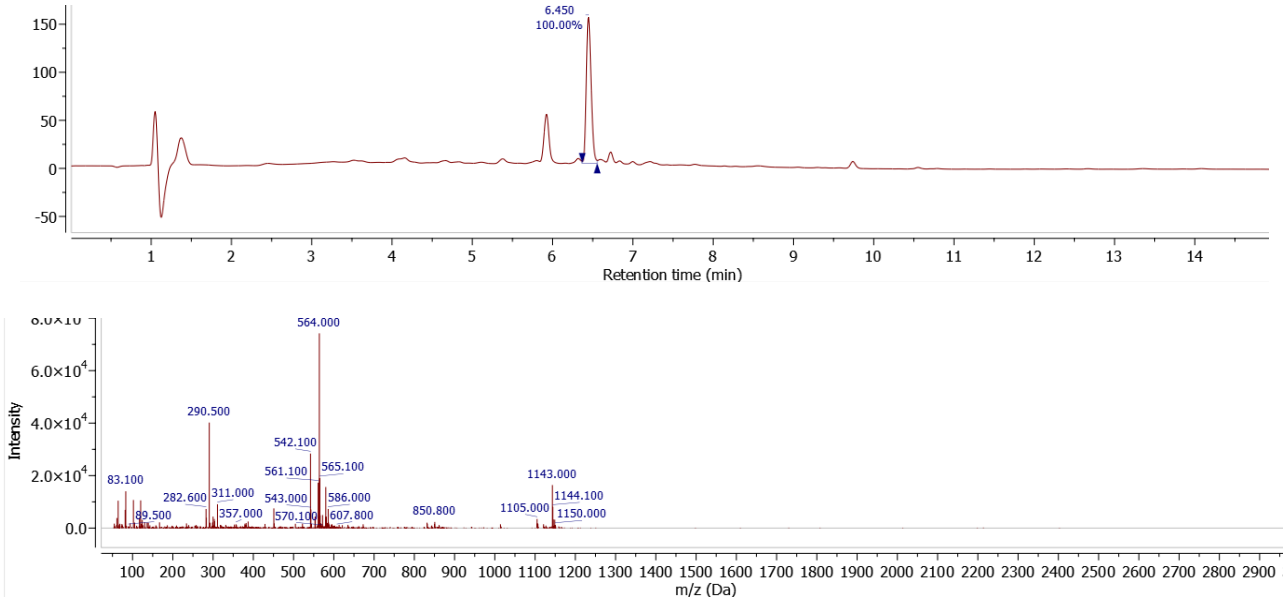


HPLC-MS analysis of **Boc-(L-Ala-D-Oxd)$_4$-OCH$_2$Py 3b**



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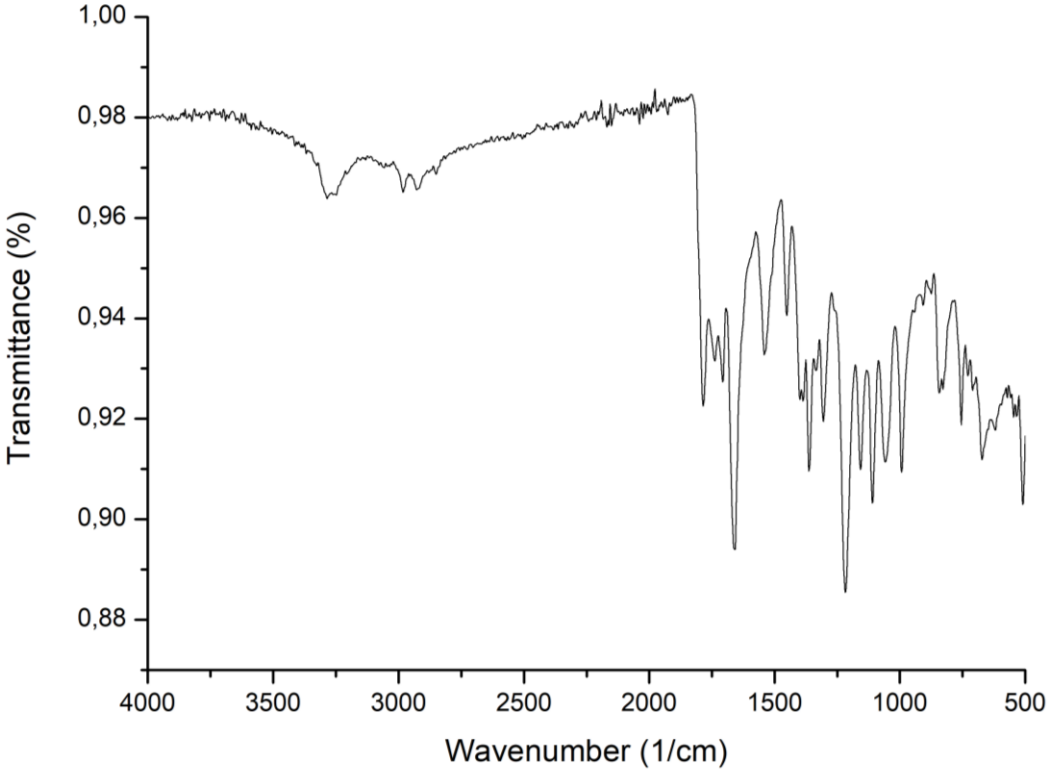
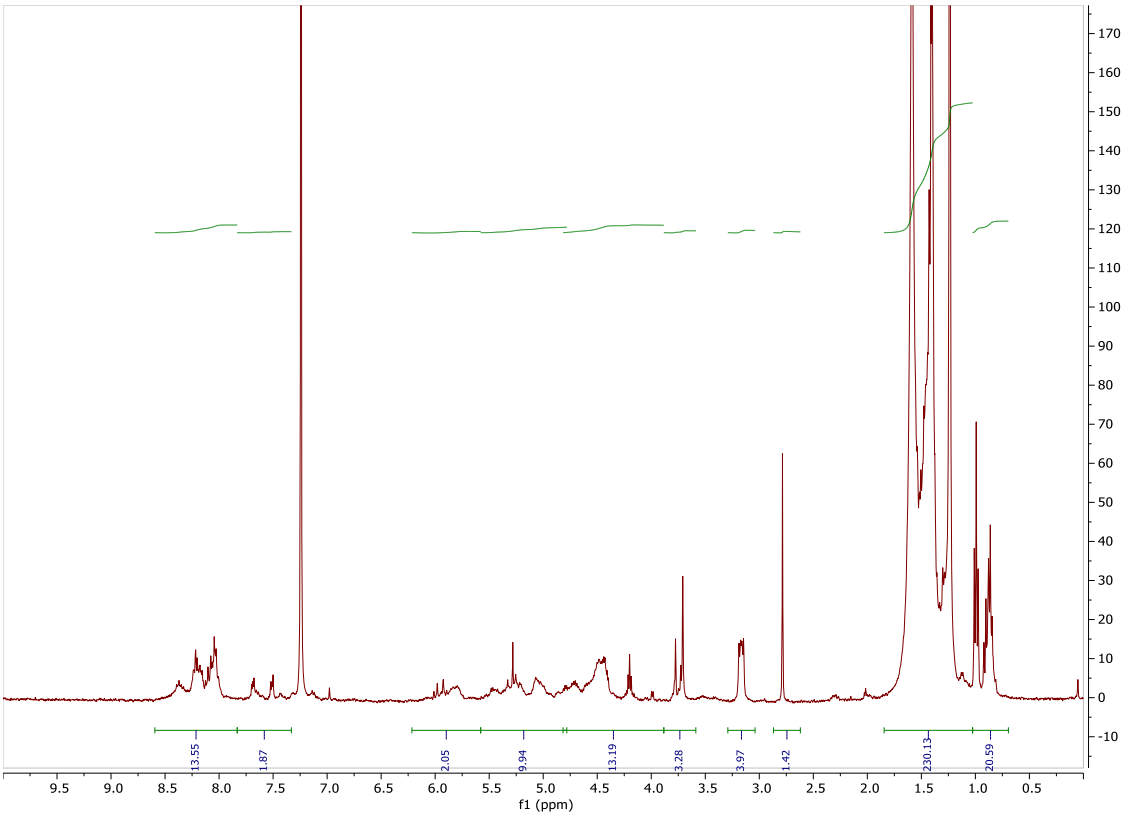
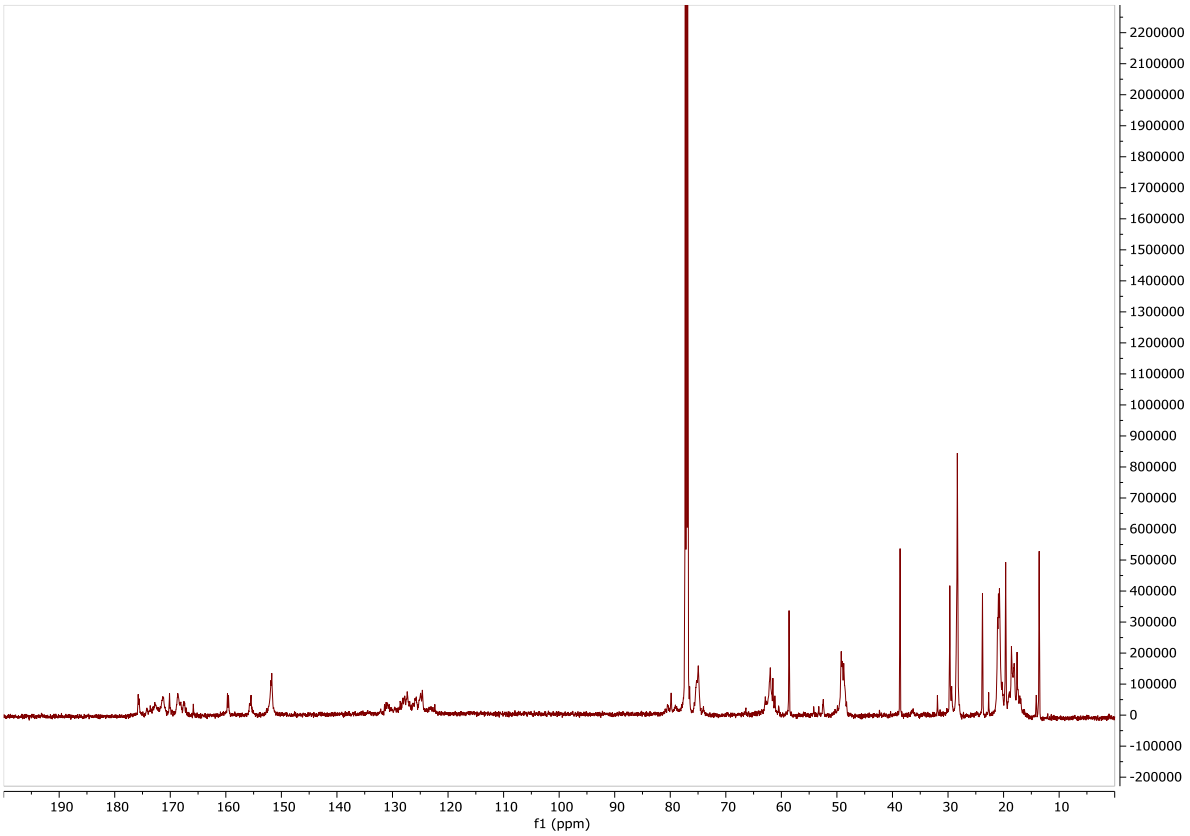
ATR-IR spectrum of **Boc-(L-Ala-D-Oxd)$_6$-OCH$_2$Py 3c**



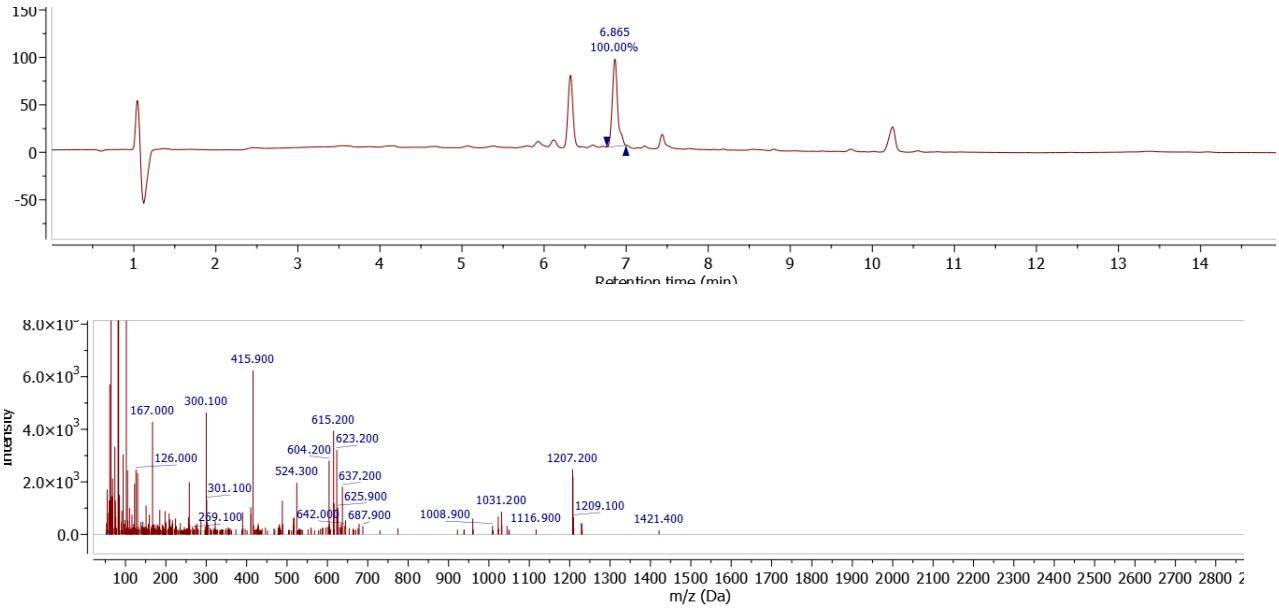
^{1}H NMR spectrum of **Boc-(L-Ala-D-Oxd)$_6$-OCH$_2$Py 3c**



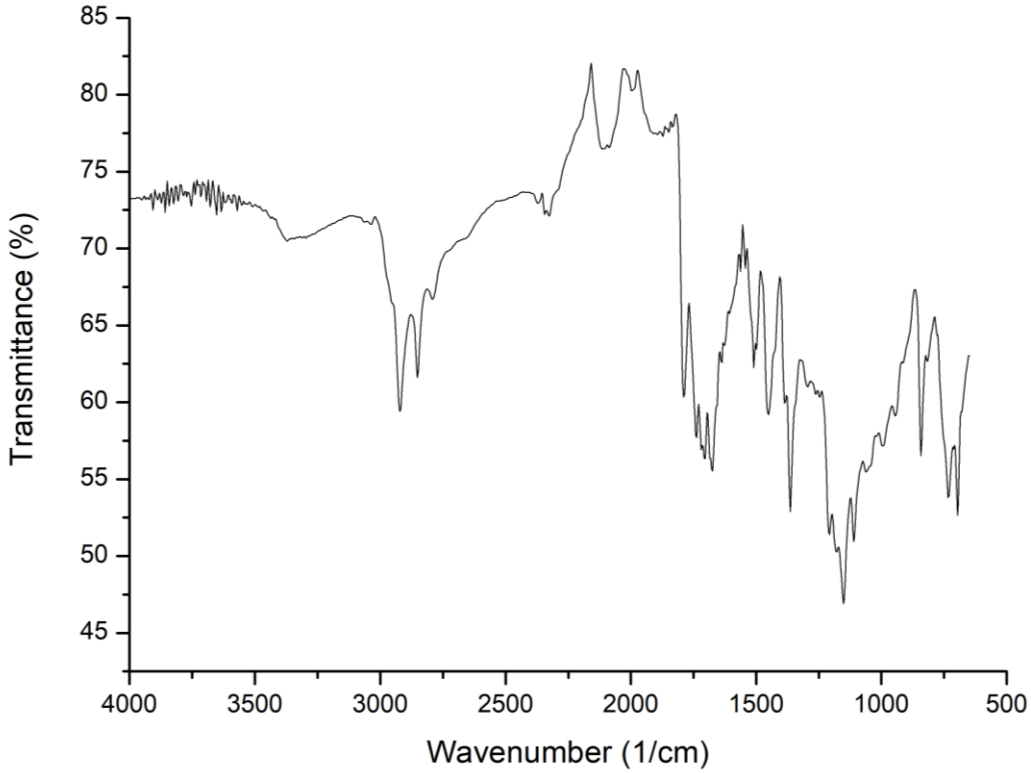
^{13}C NMR spectrum of **Boc-(L-Ala-D-Oxd)$_6$-OCH$_2$Py 3c**



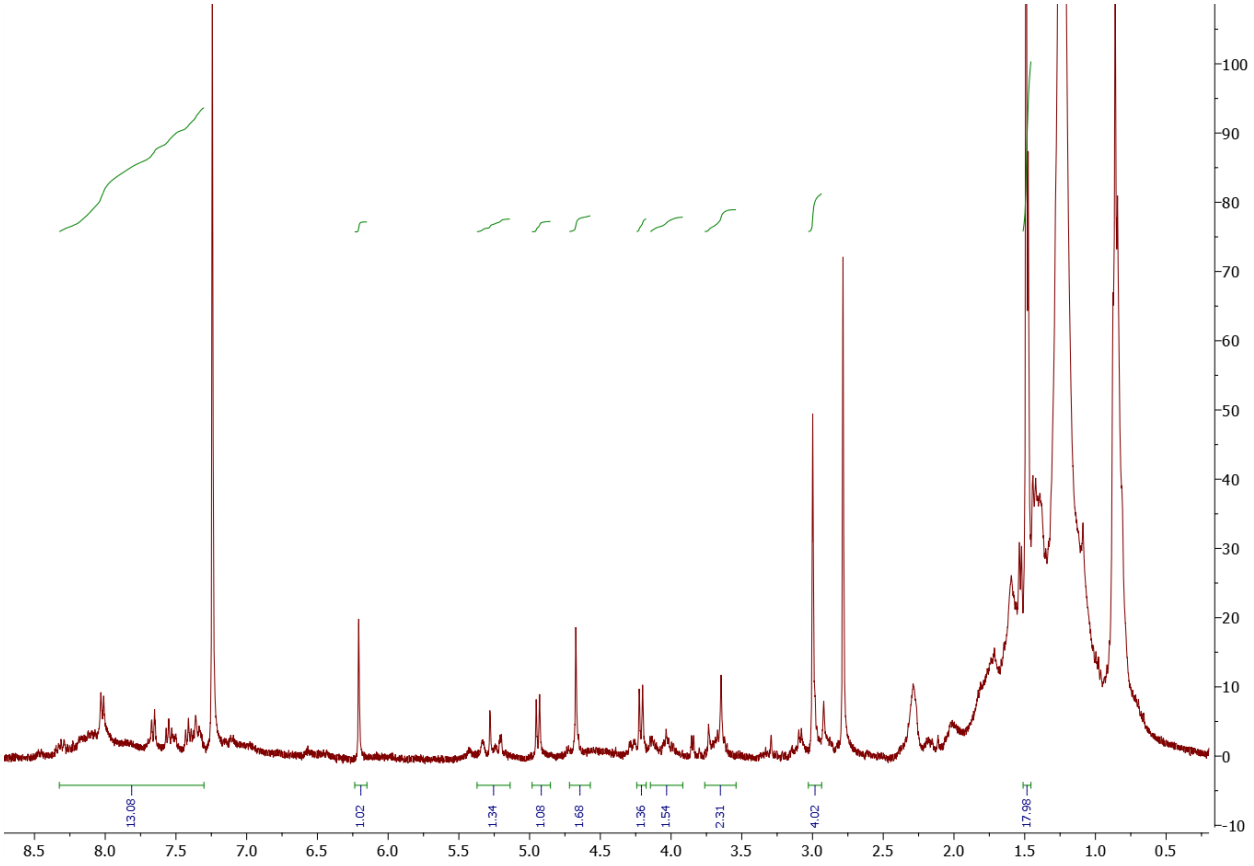
HPLC-MS analysis of **Boc-(L-Ala-D-Oxd)$_6$-OCH$_2$Py 3c**



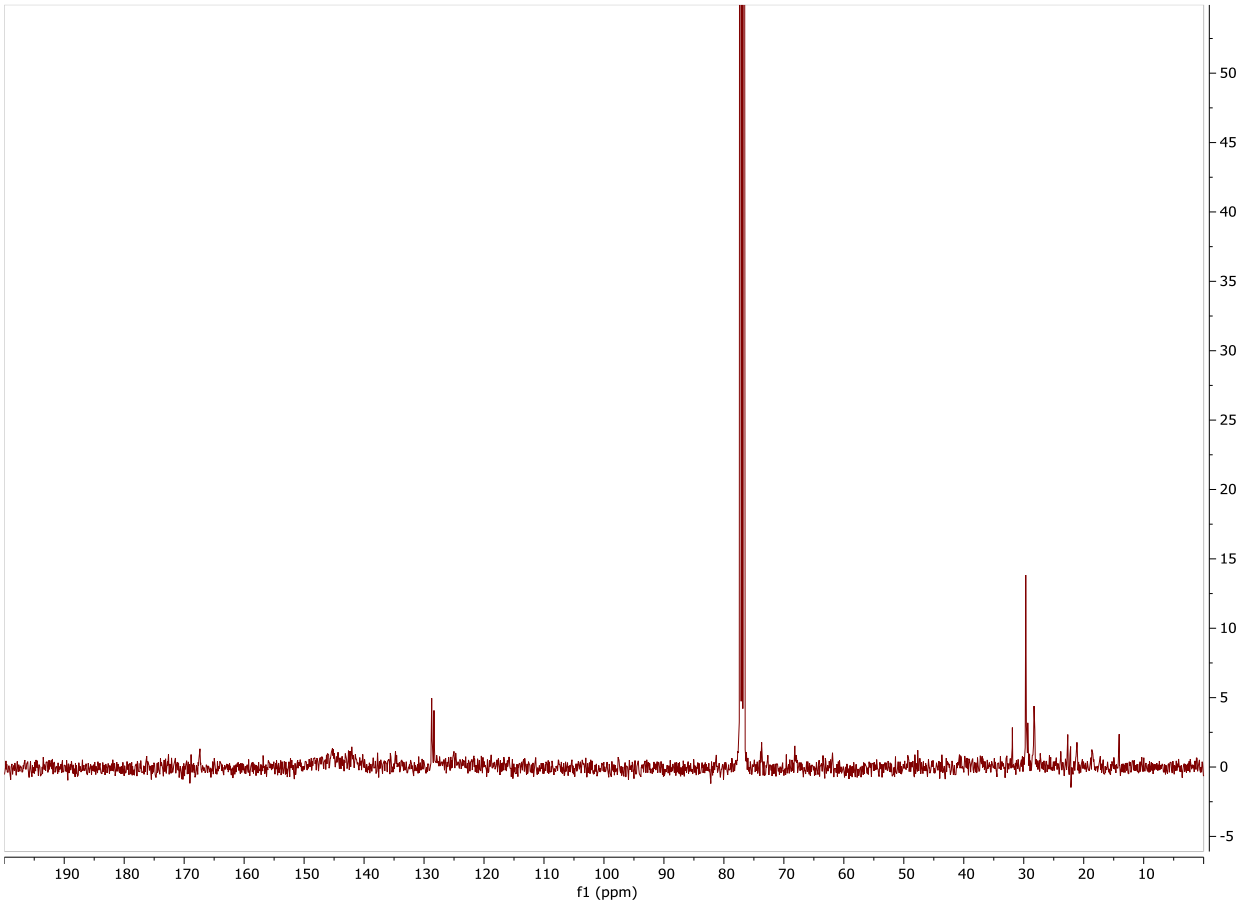
ATR-IR spectrum of **dyad Dir4**



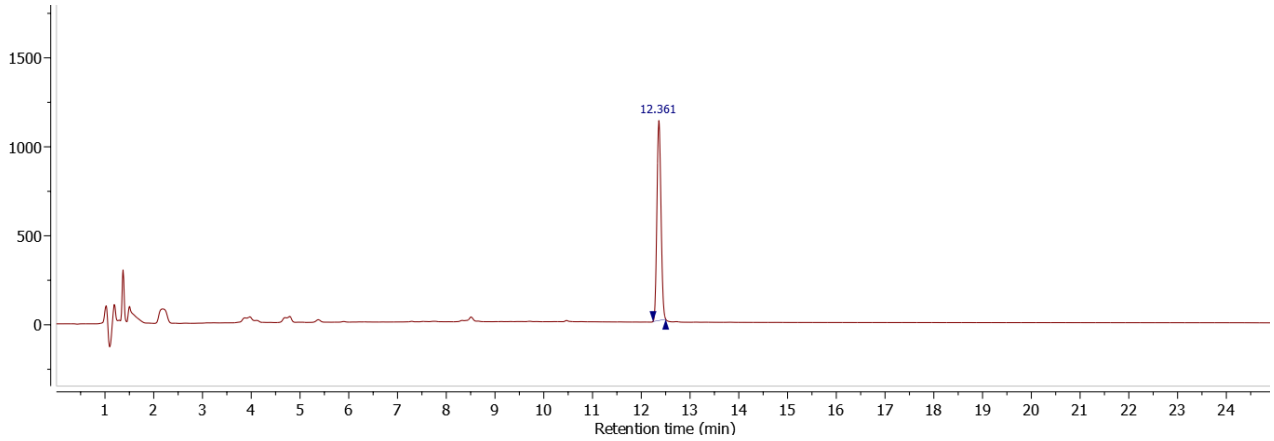
^{1}H NMR spectrum of **dyad Dir4**



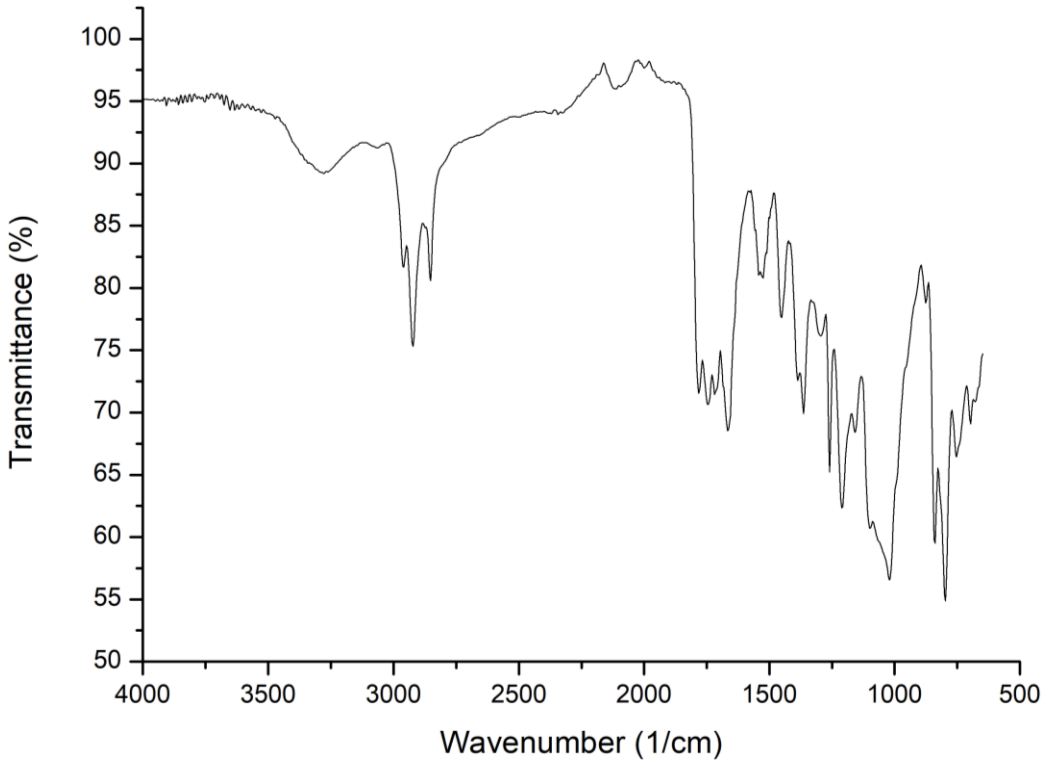
^{13}C NMR spectrum of **dyad Dir4**



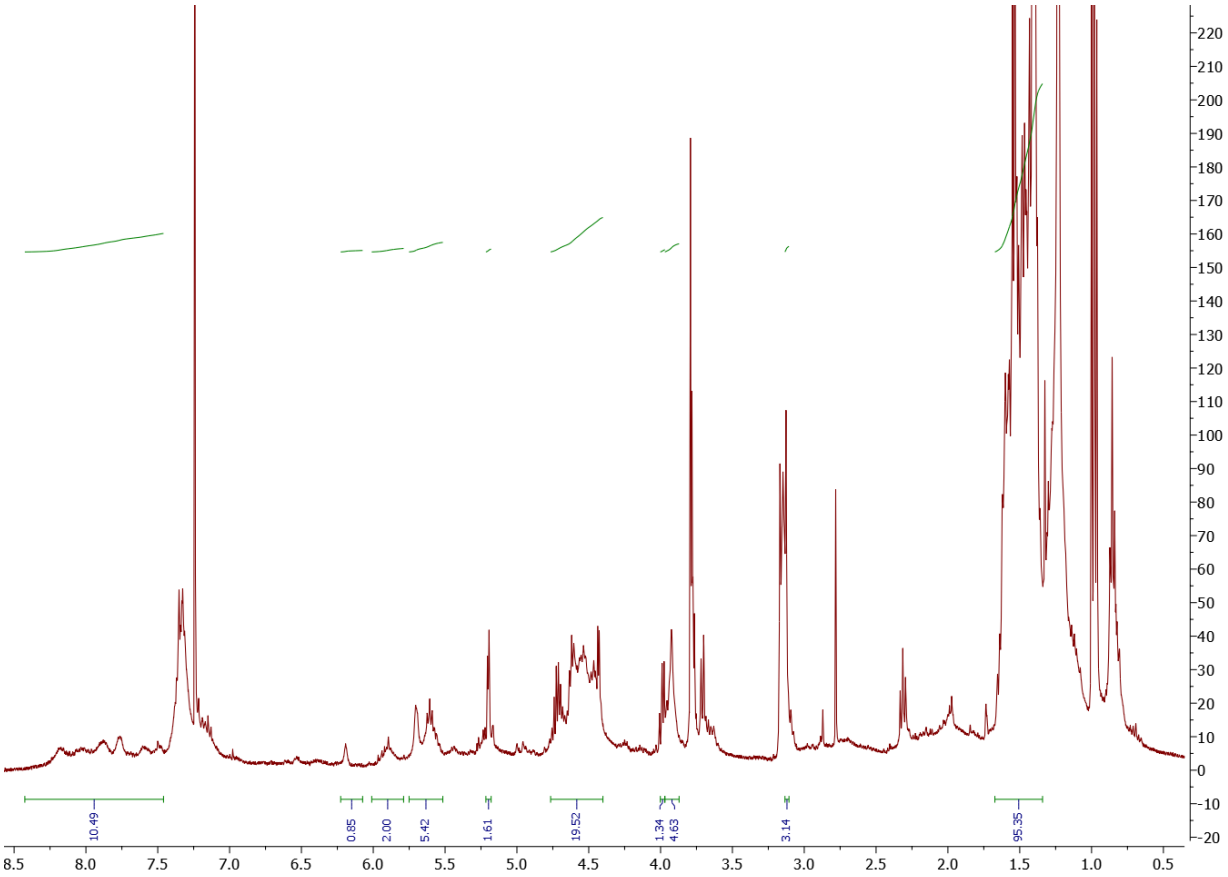
HPLC analysis of **dyad Dir4**



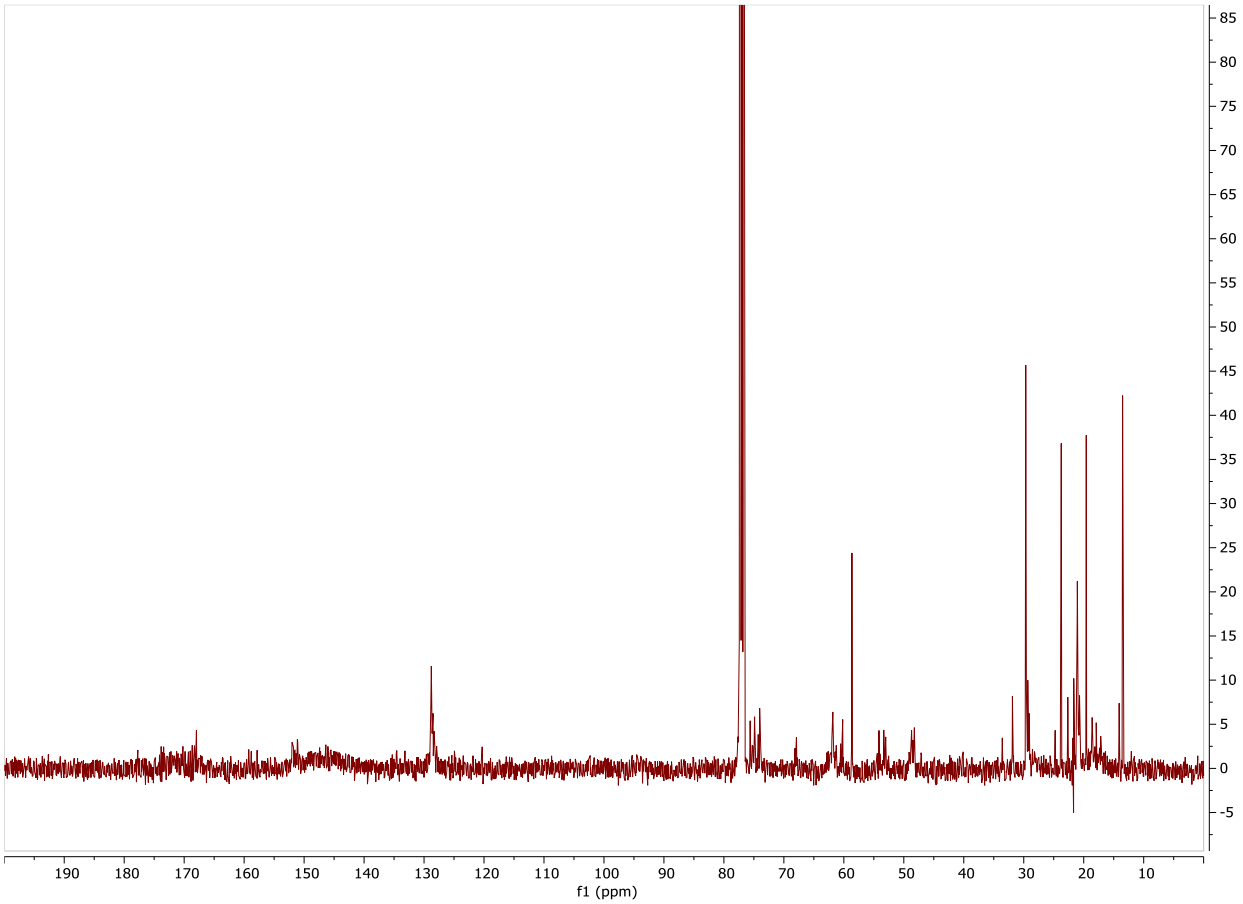
ATR-IR spectrum of **dyad Dir10**



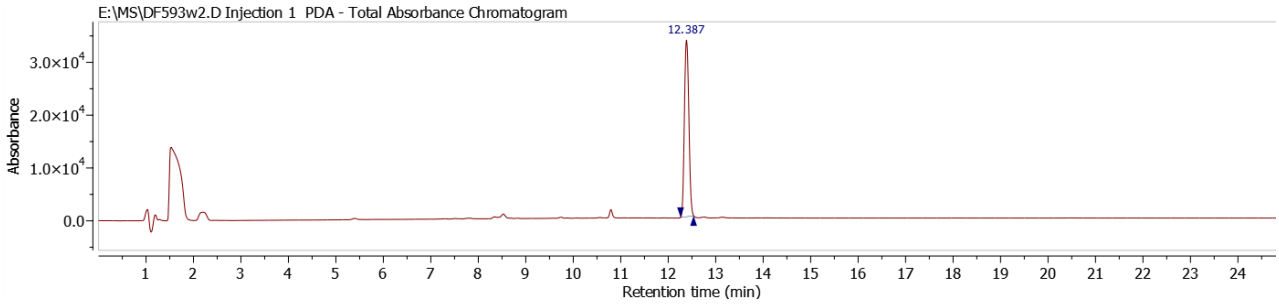
^{1}H NMR spectrum of **dyad Dir10**



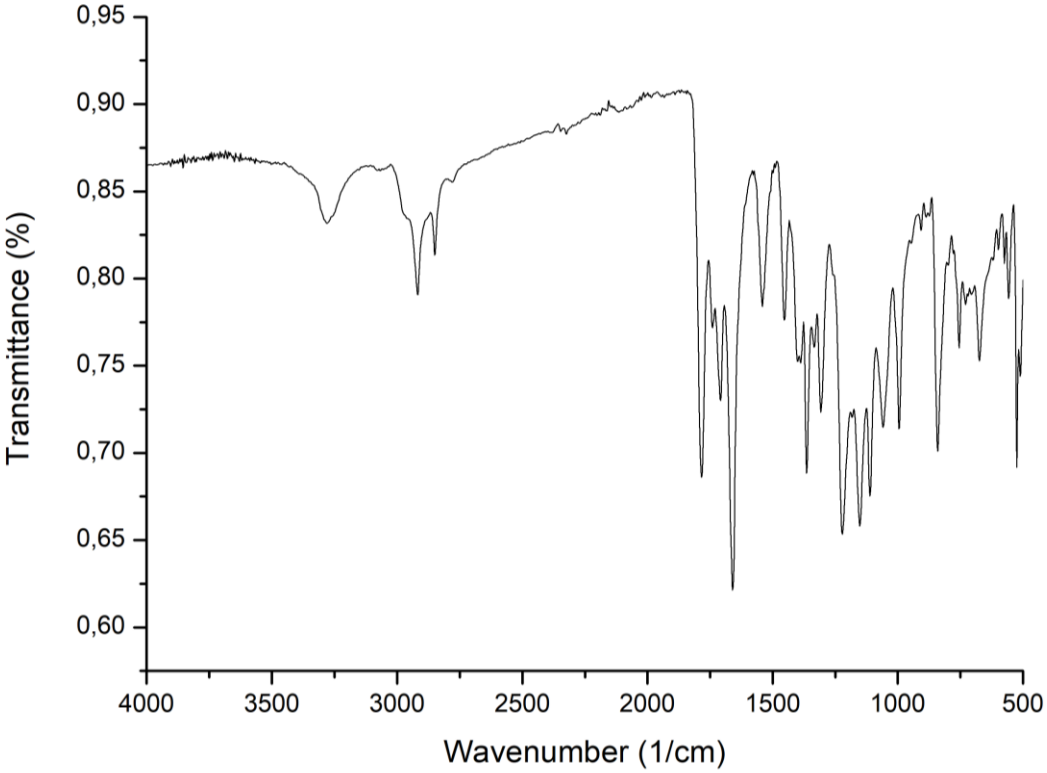
^{13}C NMR spectrum of **dyad Dir10**



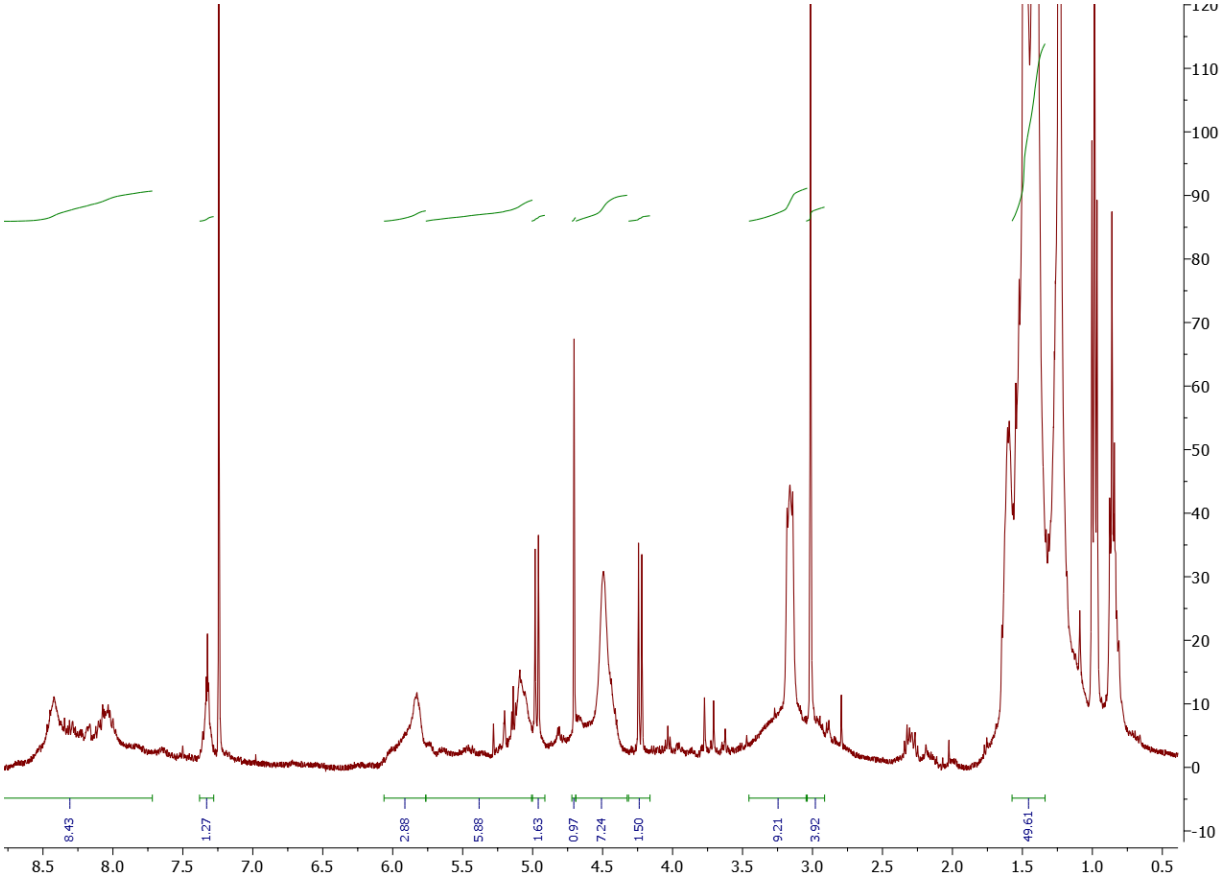
HPLC analysis of **dyad Dir10**



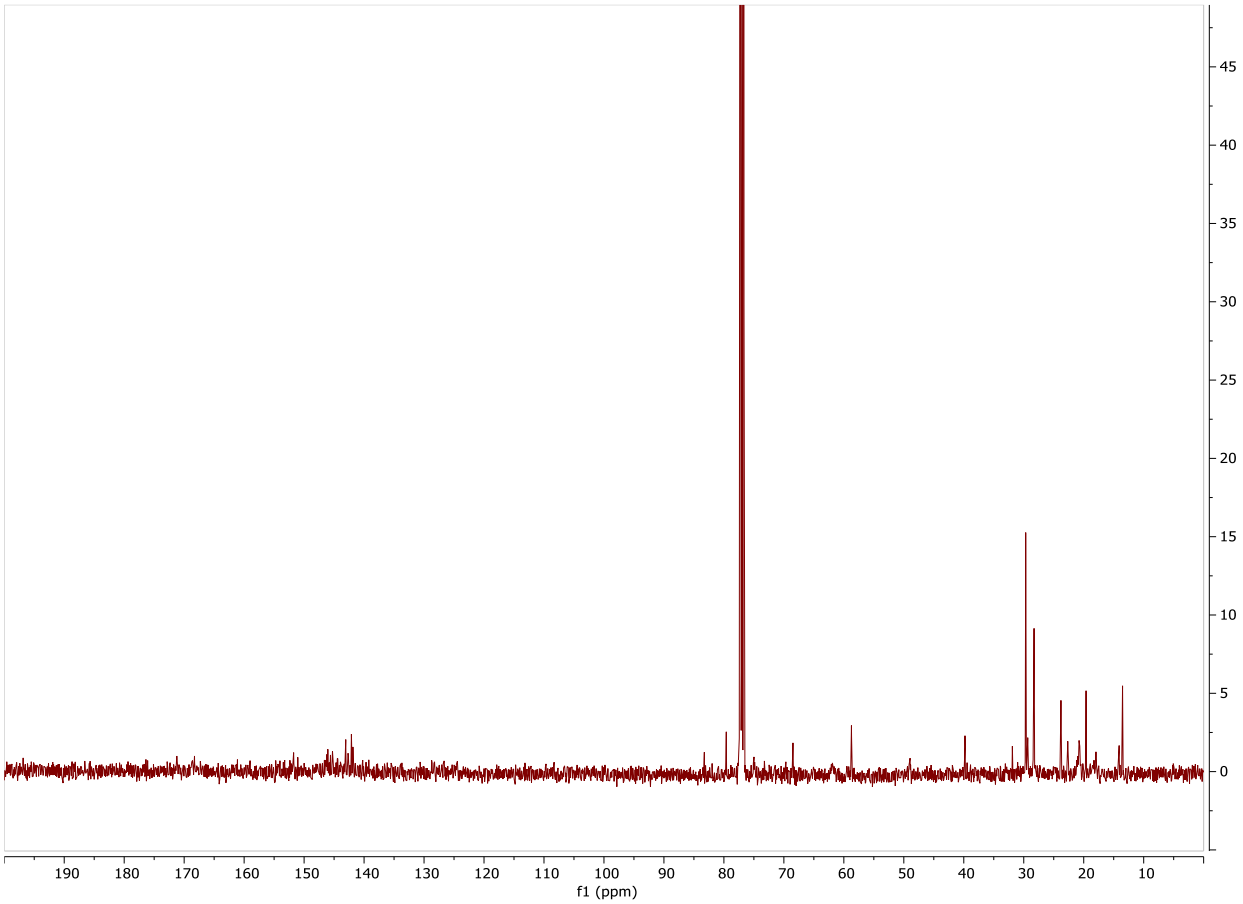
ATR-IR spectrum of **dyad Dir14**



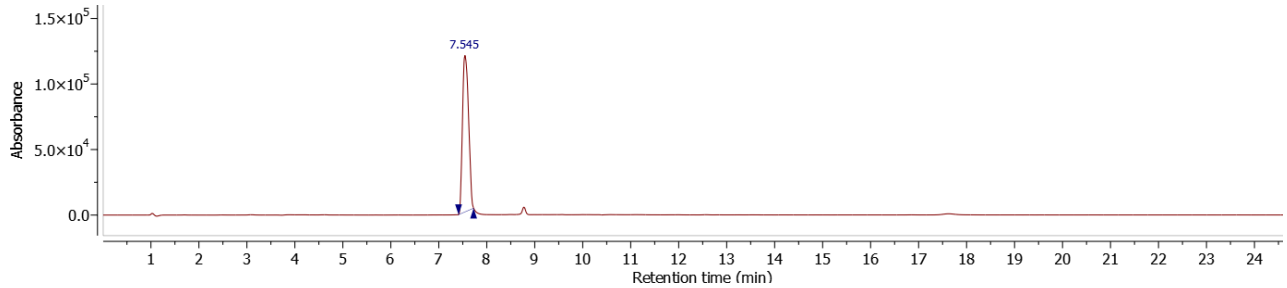
^{1}H NMR spectrum of **dyad Dir14**



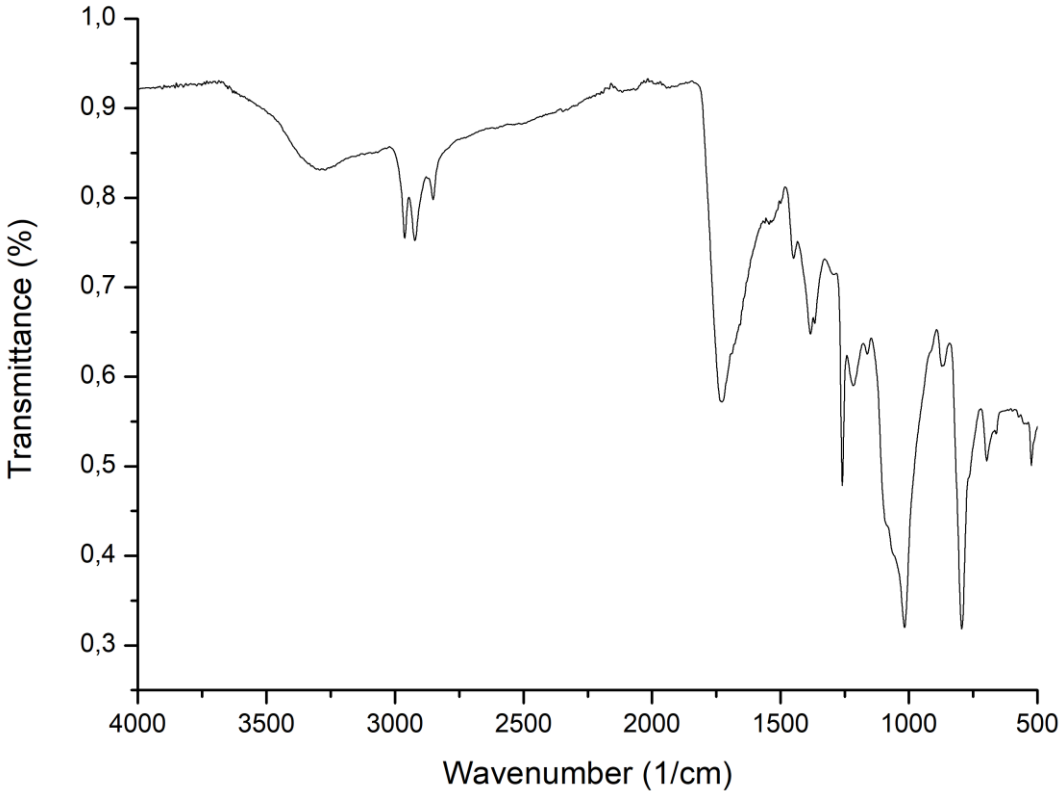
^{13}C NMR spectrum of **dyad Dir14**



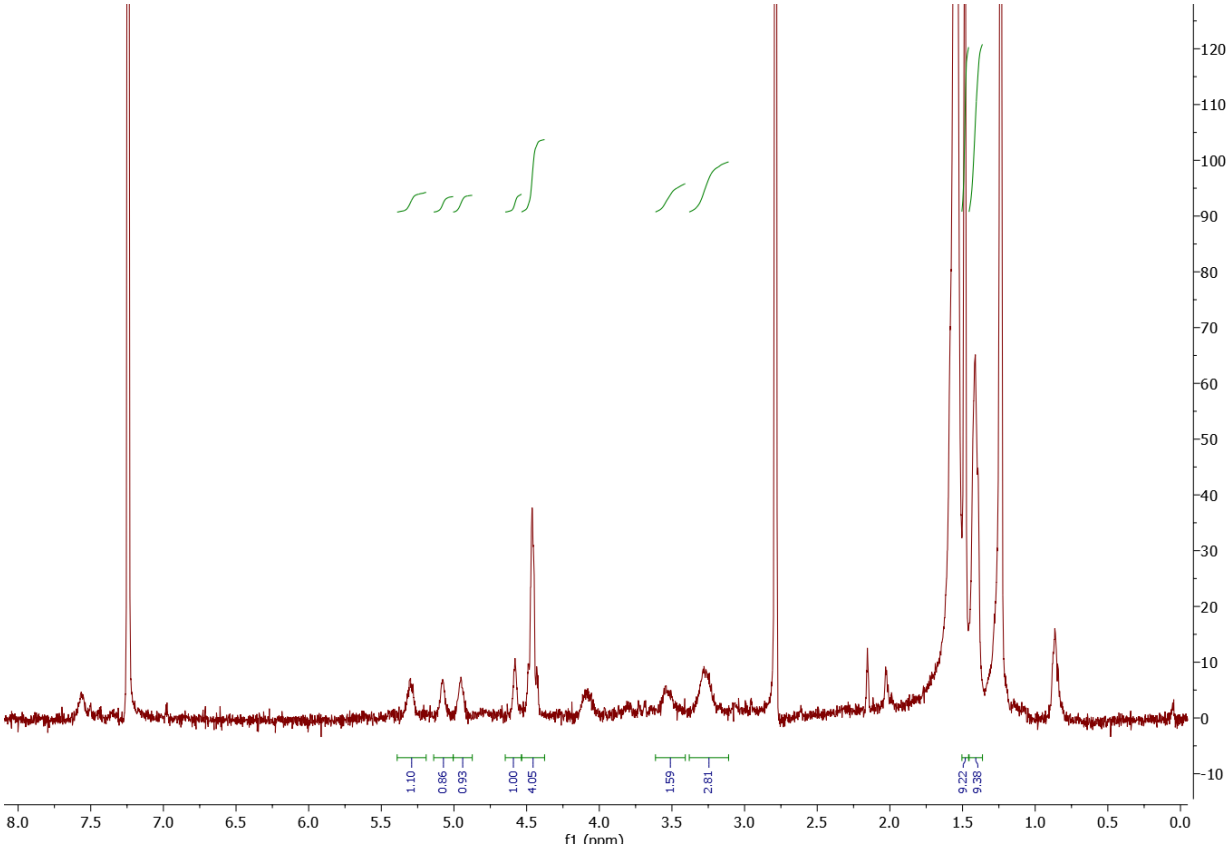
HPLC analysis of **dyad Dir14**



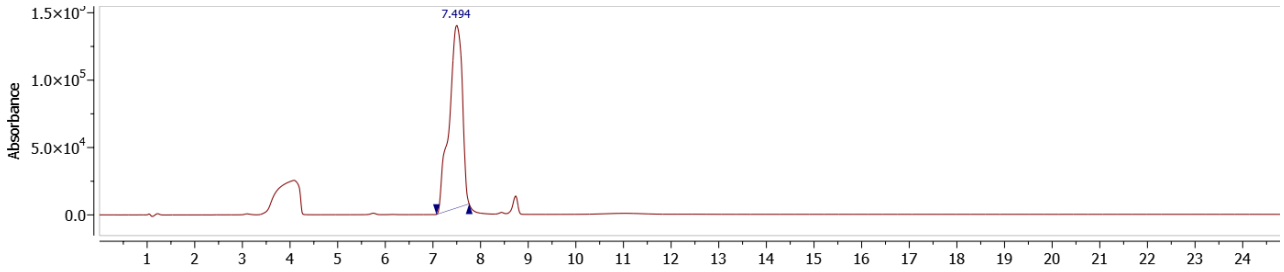
ATR-IR spectrum of **Boc-L-Ala-D-Oxd-*N*-2-aminoethyl-*N*-Fpyrr 4**



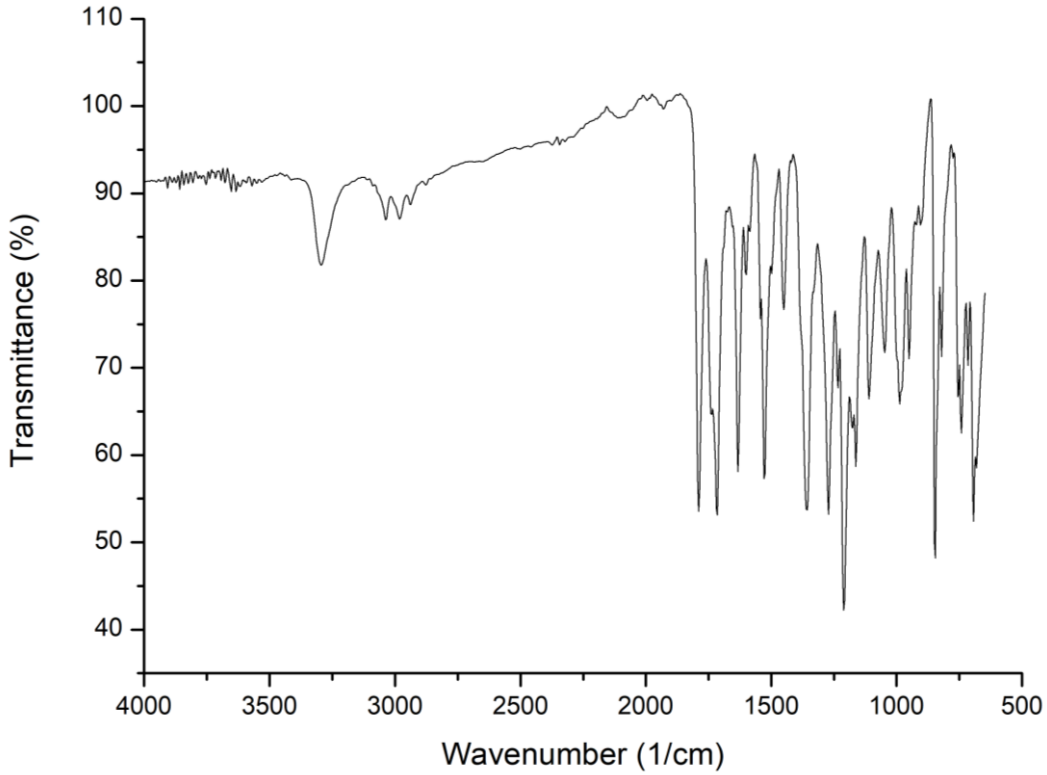
^{1}H NMR spectrum of **Boc-L-Ala-D-Oxd-*N*-2-aminoethyl-*N*-Fpyrr 4**



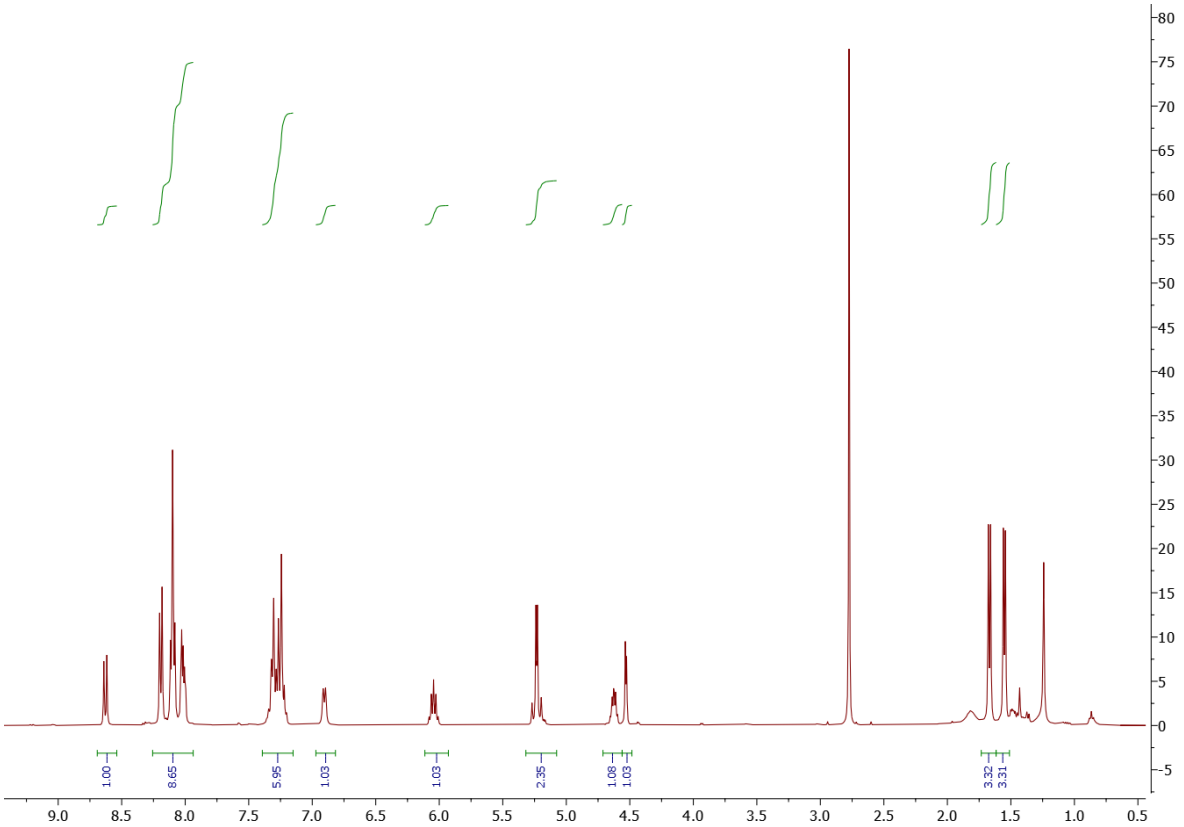
HPLC of **Boc-L-Ala-D-Oxd-*N*-2-aminoethyl-*N*-Fpyrr 4**



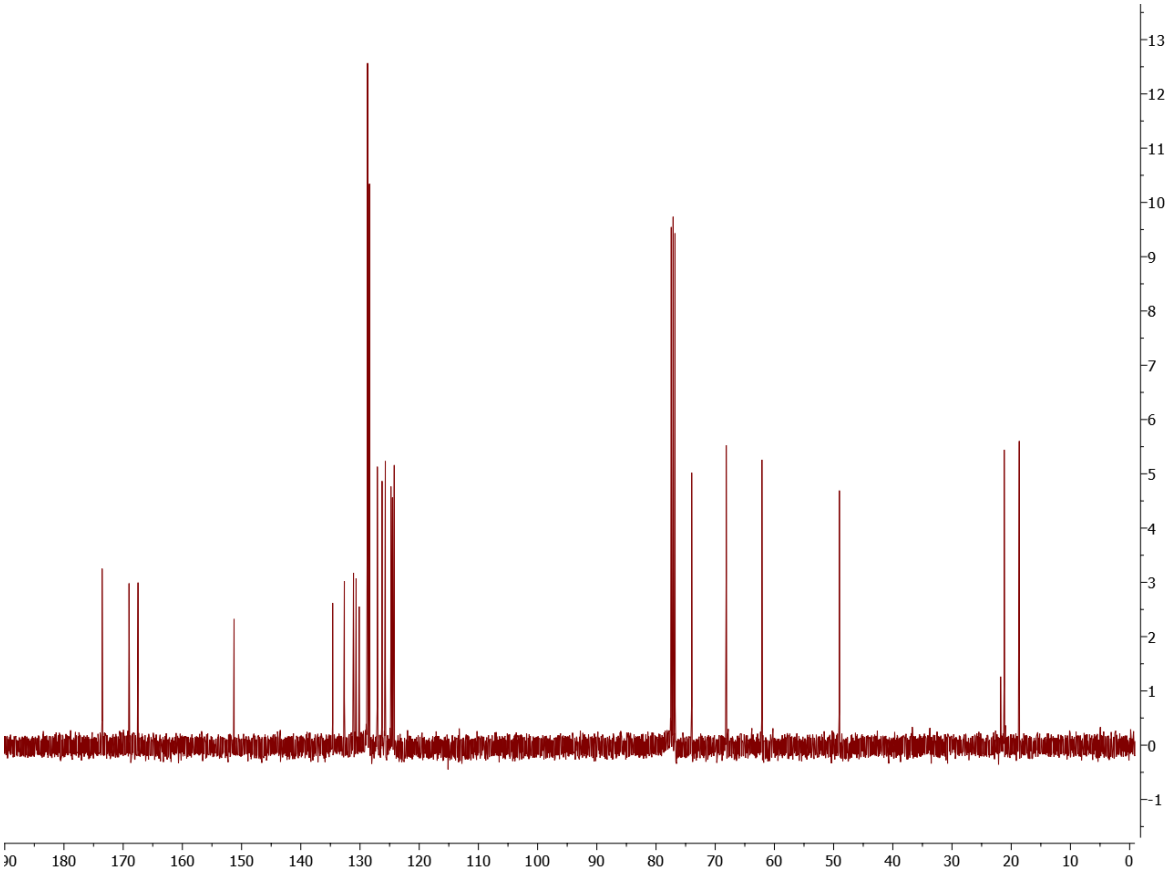
ATR-IR spectrum of **PyCO-L-Ala-D-Oxd-OBn 5a Py-Inv**



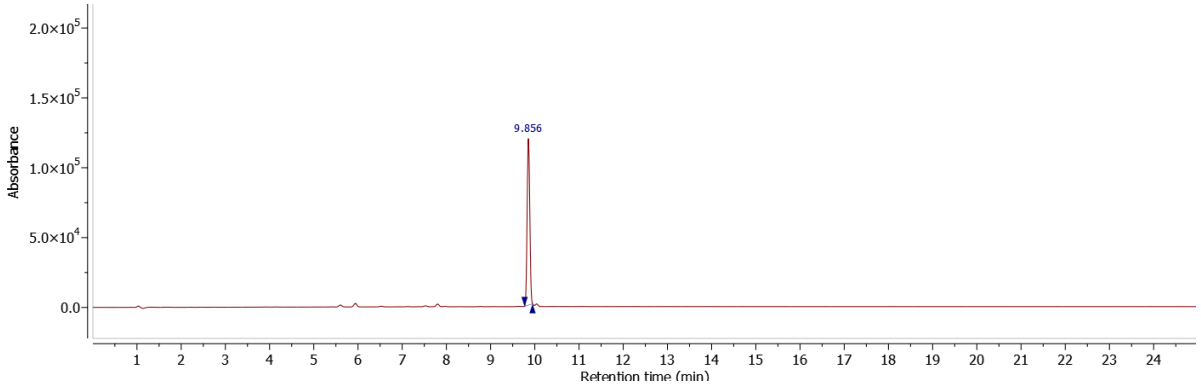
^{1}H NMR spectrum of **PyCO-L-Ala-D-Oxd-OBn 5a Py-Inv**

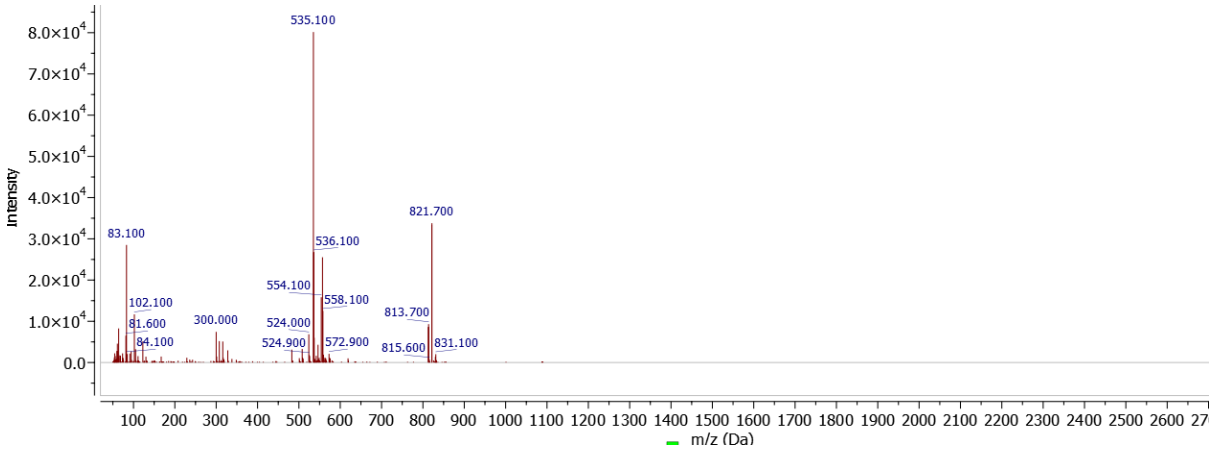


^{13}C NMR spectrum of **PyCO-L-Ala-D-Oxd-OBn 5a Py-Inv**

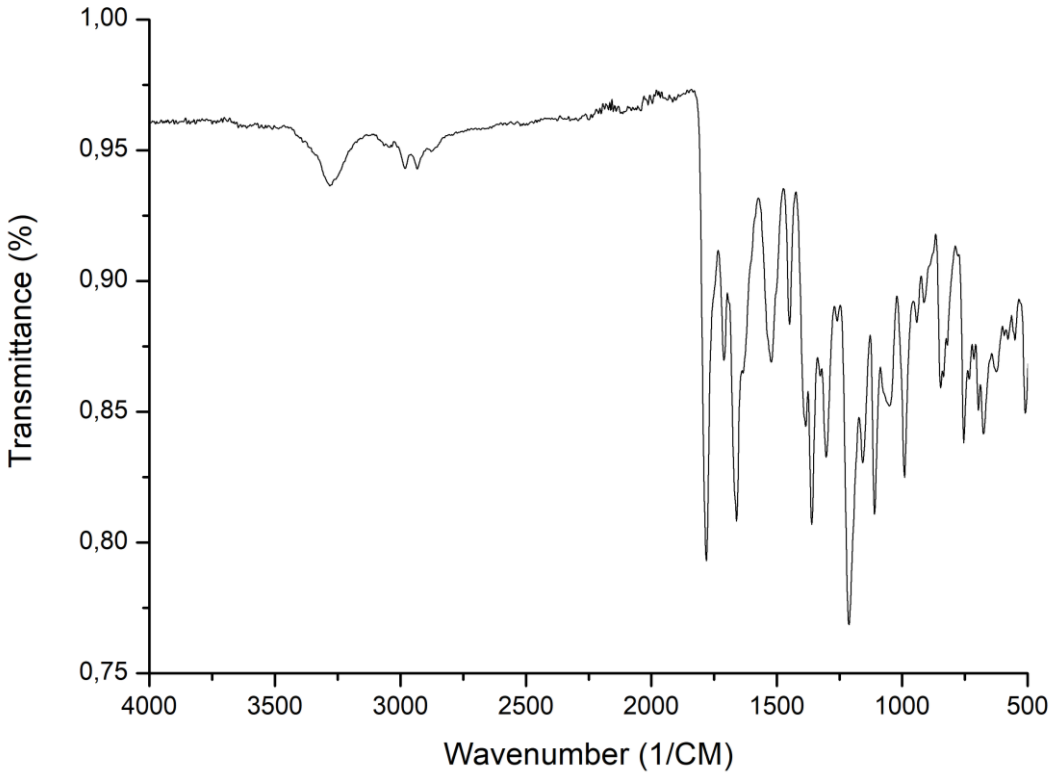


HPLC-MS analysis of **PyCO-L-Ala-D-Oxd-OBn 5a Py-Inv**

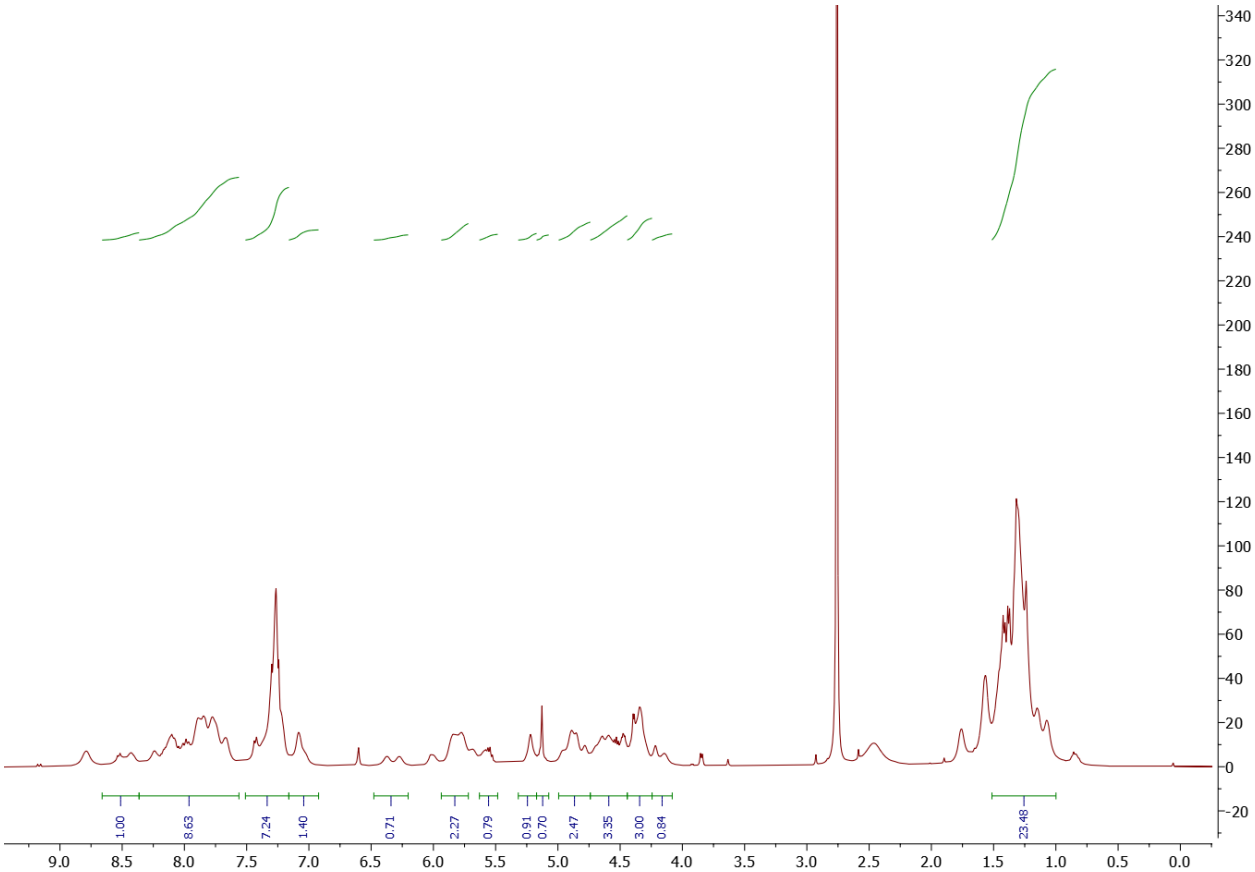




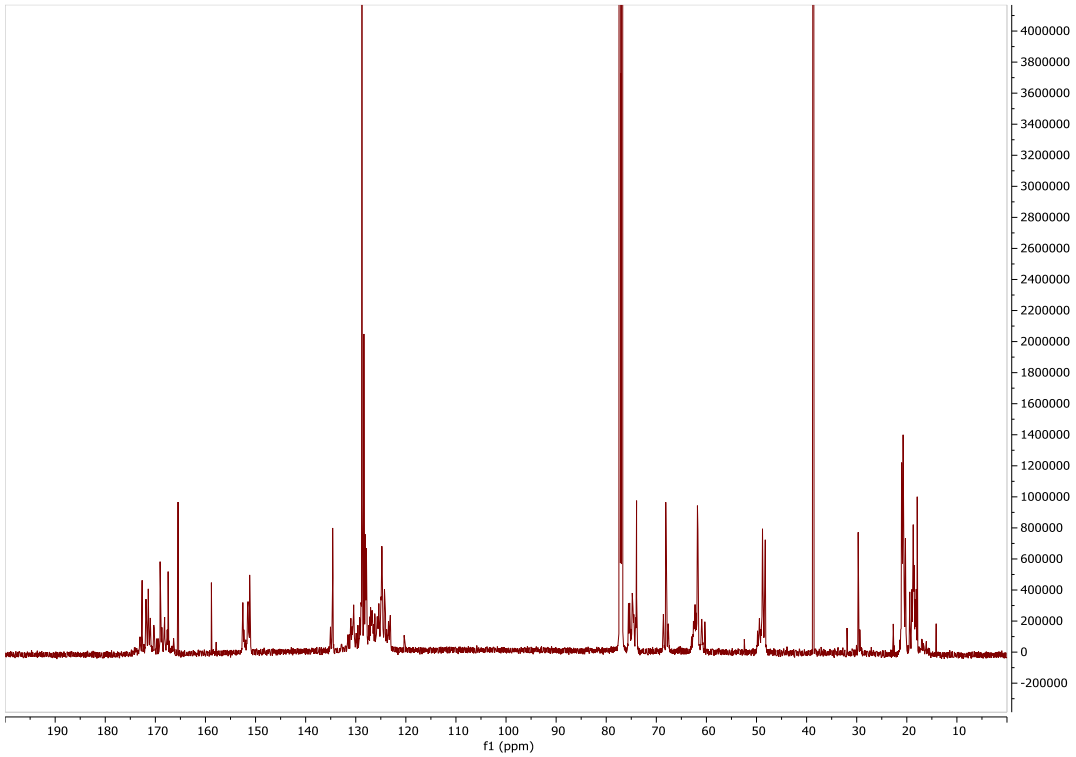
ATR-IR spectrum of **PyCO-(L-Ala-D-Oxd)$_4$-OBn 5b**



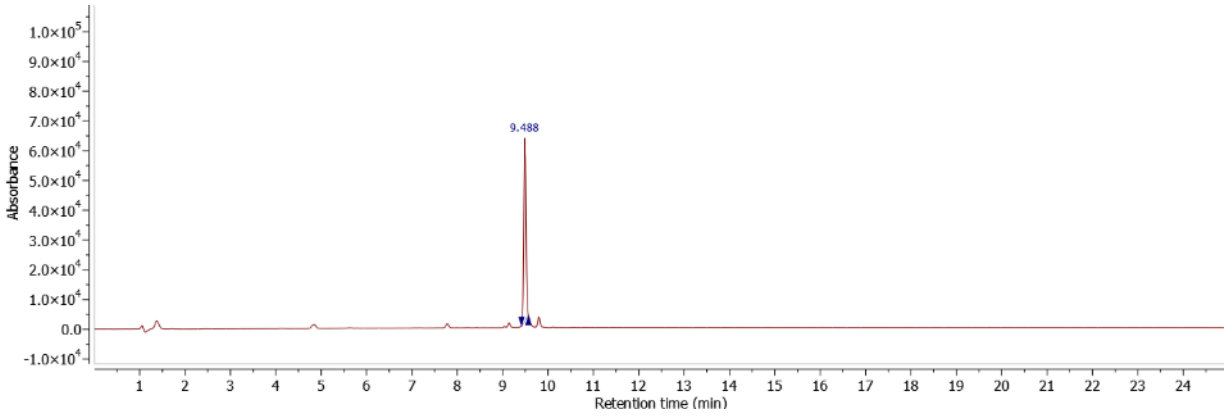
^{1}H NMR spectrum of **PyCO-(L-Ala-D-Oxd)$_4$-OBn 5b**

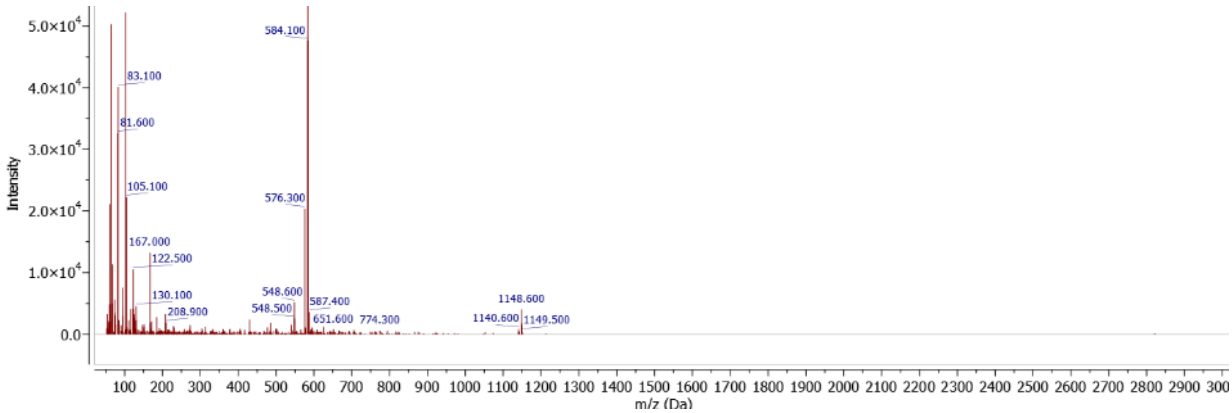


^{13}C NMR spectrum of **PyCO-(L-Ala-D-Oxd)$_4$-OBn 5b**

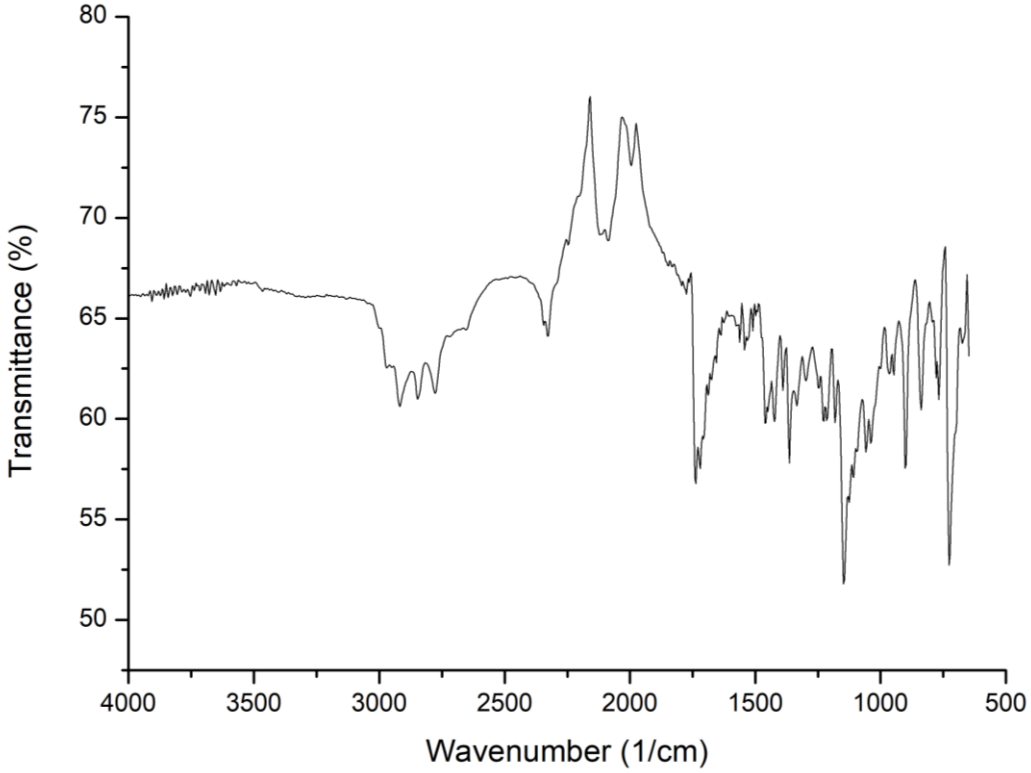


HPLC-MS analysis of **PyCO-(L-Ala-D-Oxd)$_4$-OBn 5b**

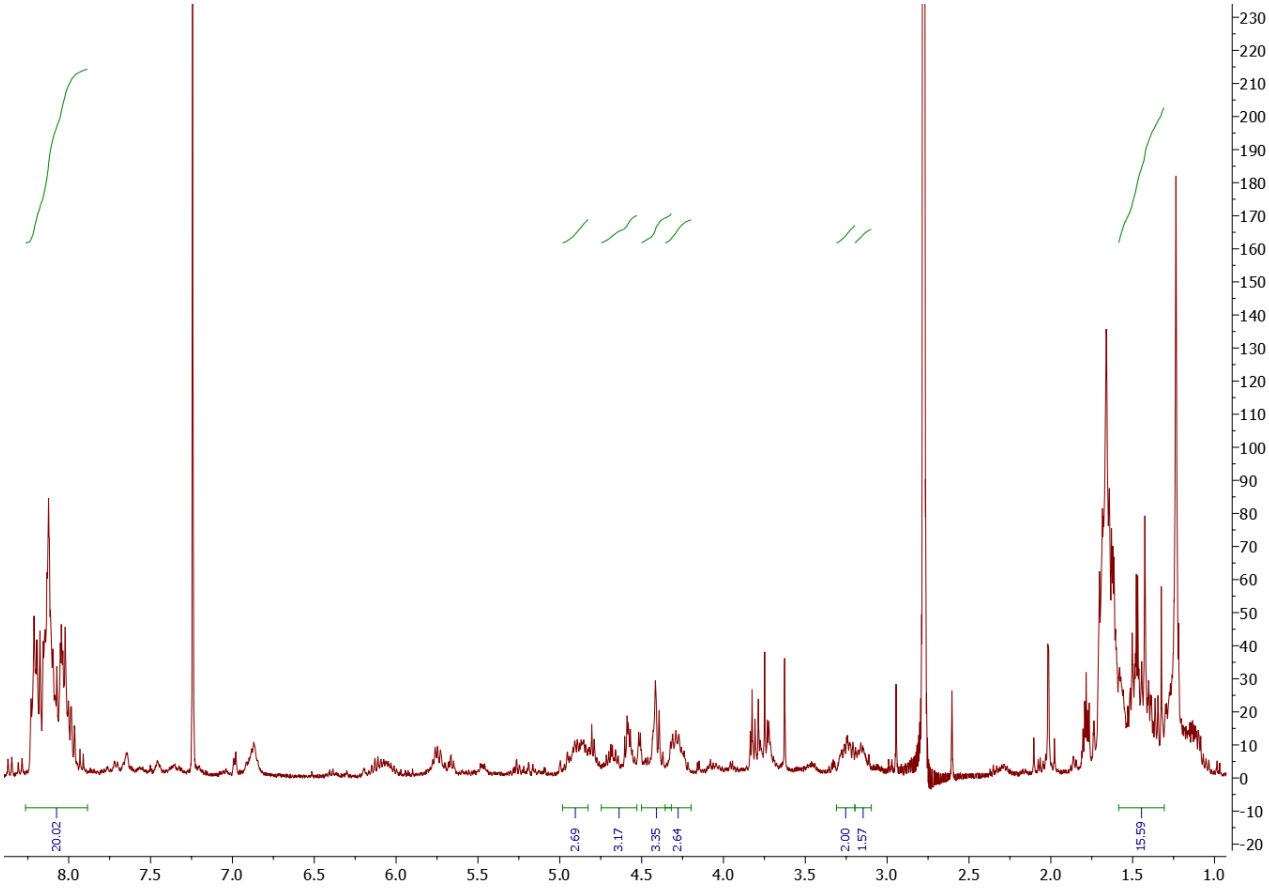




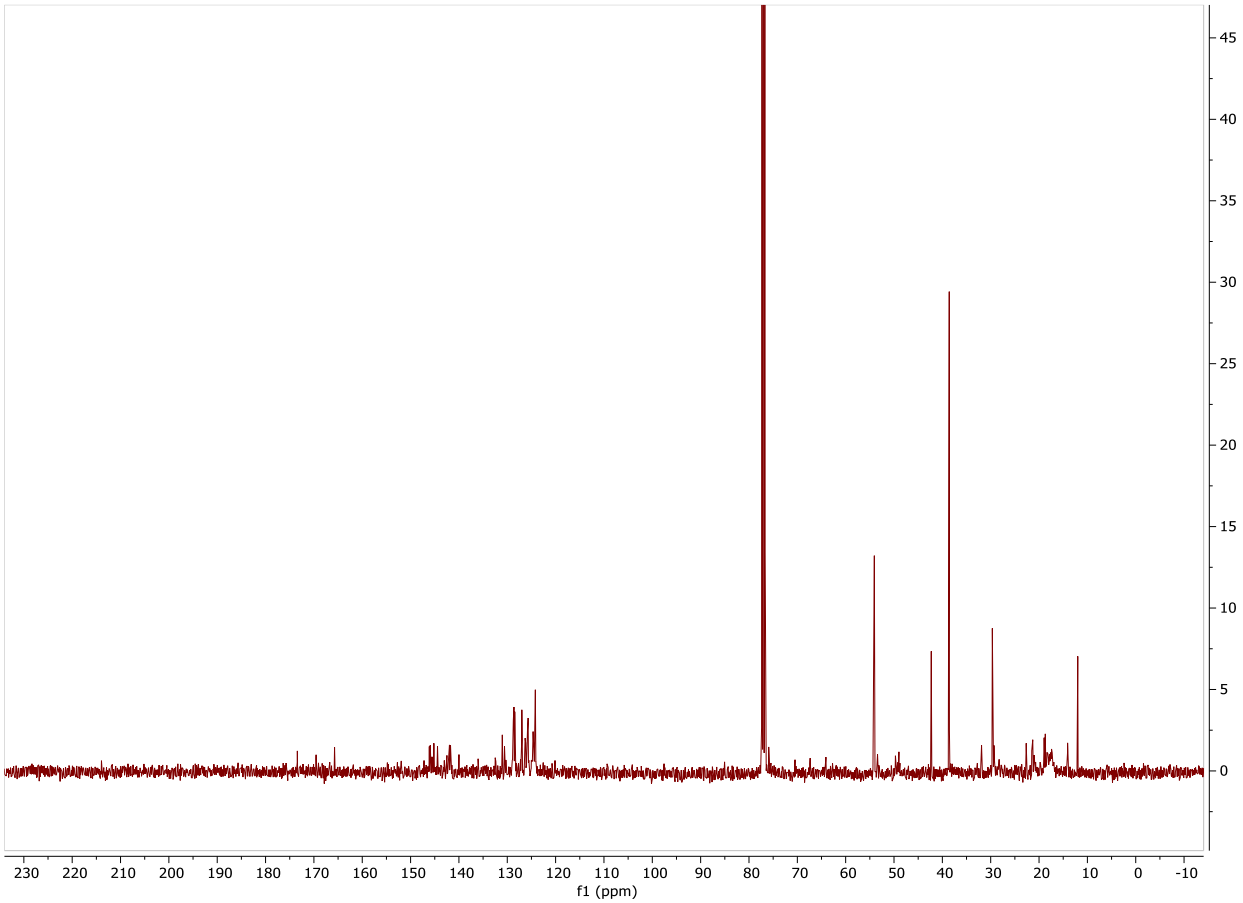
ATR-IR spectrum of **dyad Inv4**



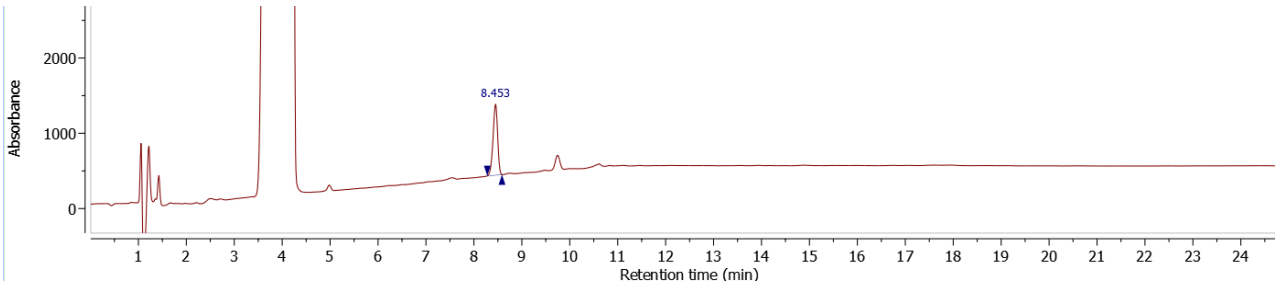
^{1}H NMR spectrum of **dyad Inv4**



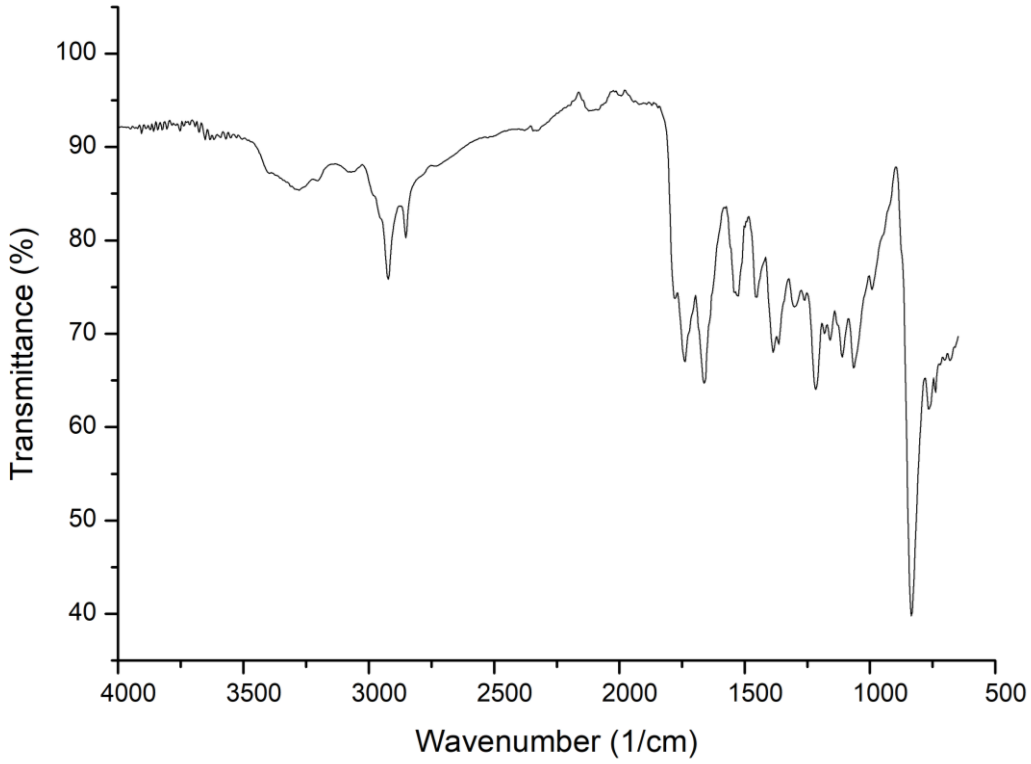
^{13}C NMR spectrum of **dyad Inv4**



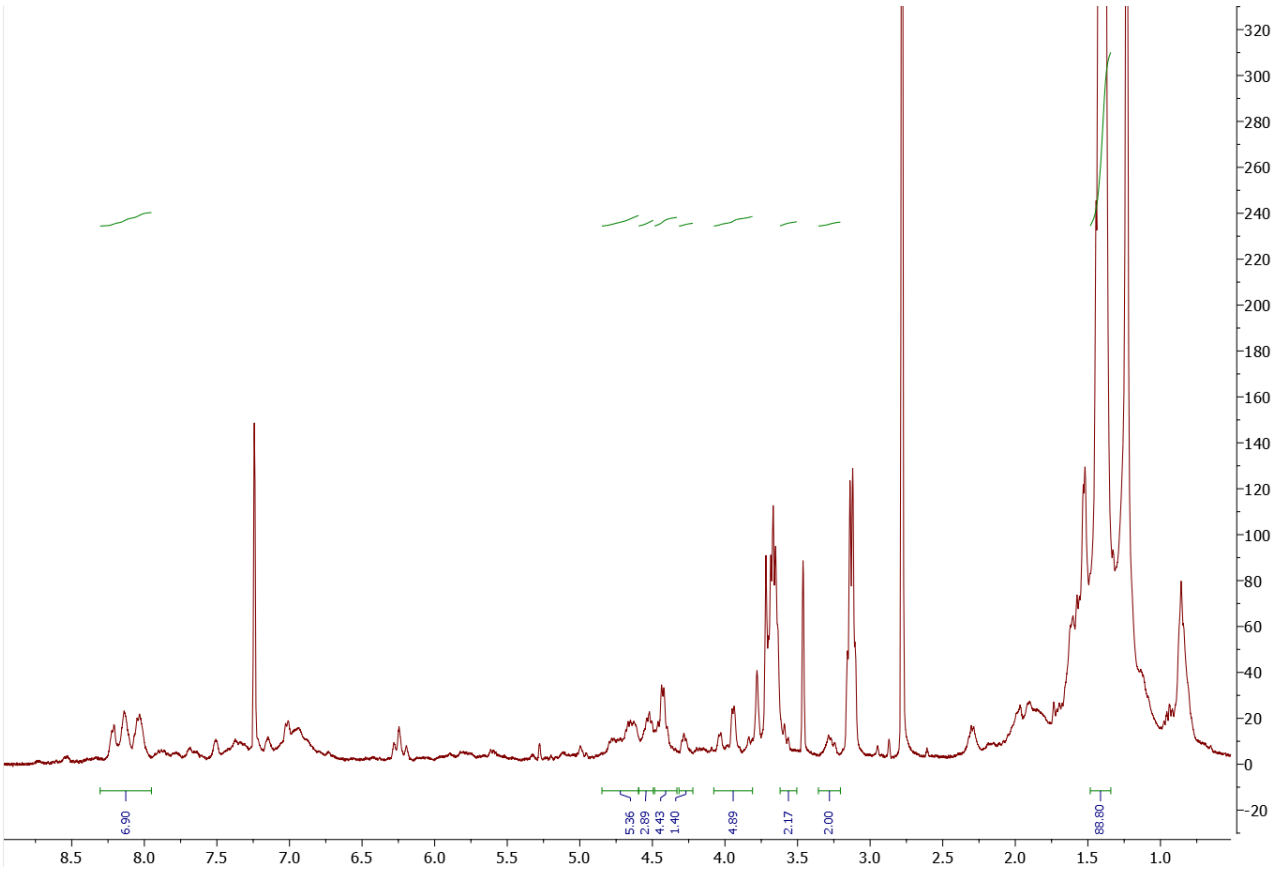
HPLC analysis of **dyad Inv4**



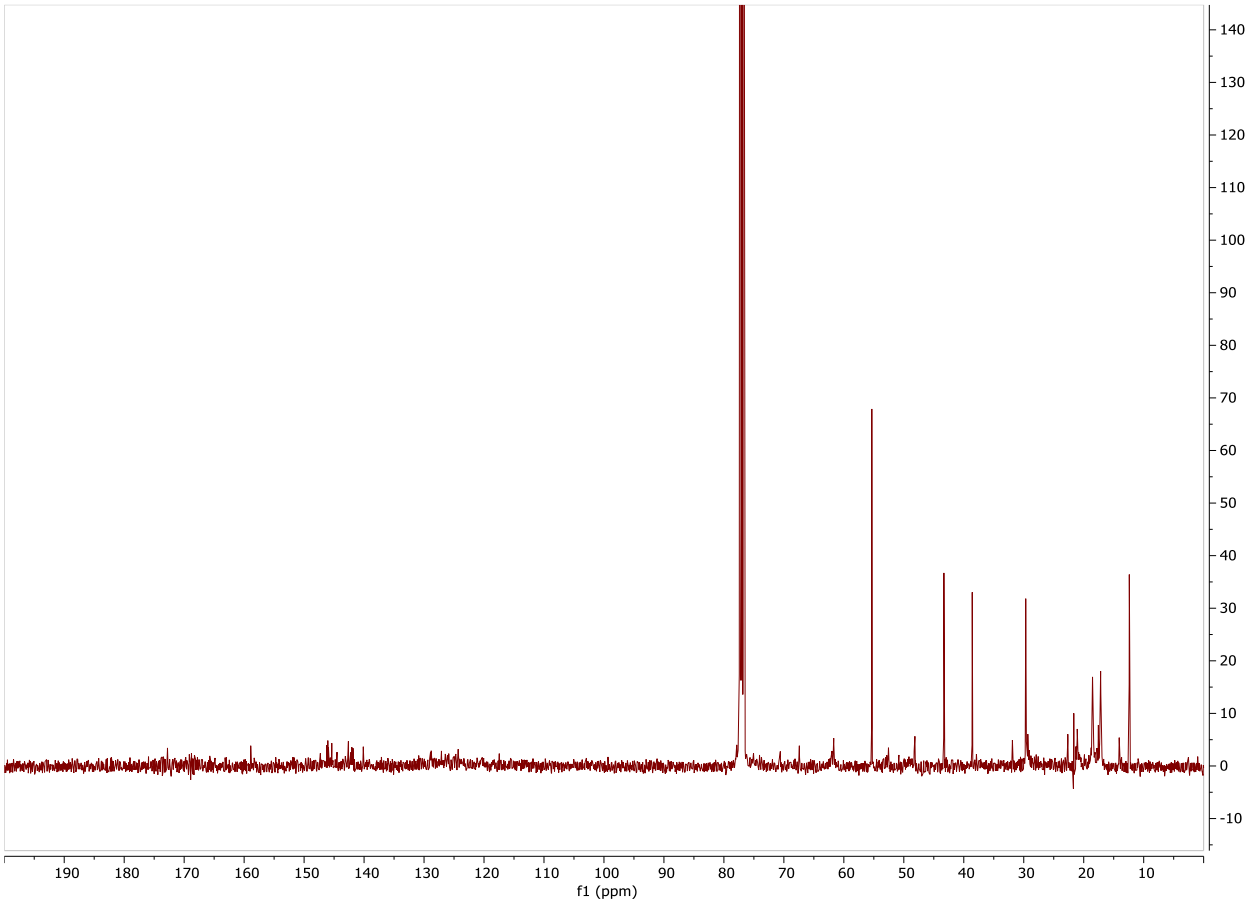
ATR-IR spectrum of **dyad Inv10**



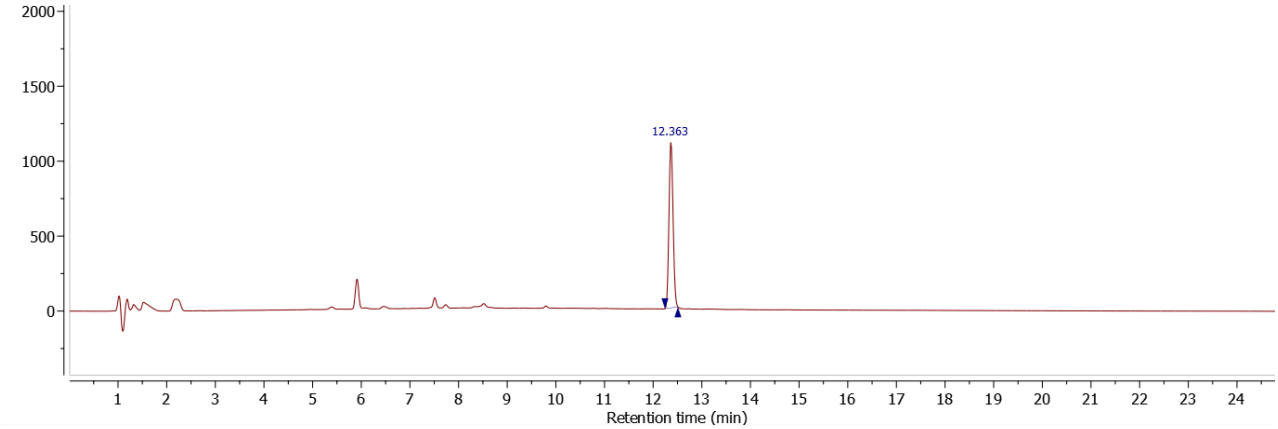
^{1}H NMR spectrum of **dyad Inv10**



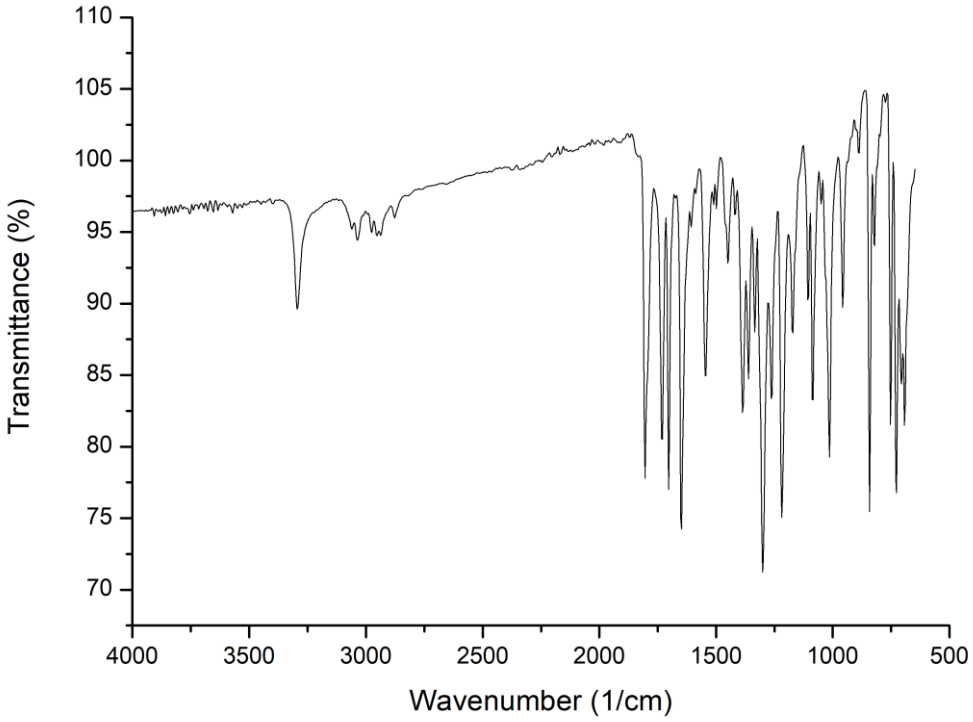
^{13}C NMR spectrum of **dyad Inv10**



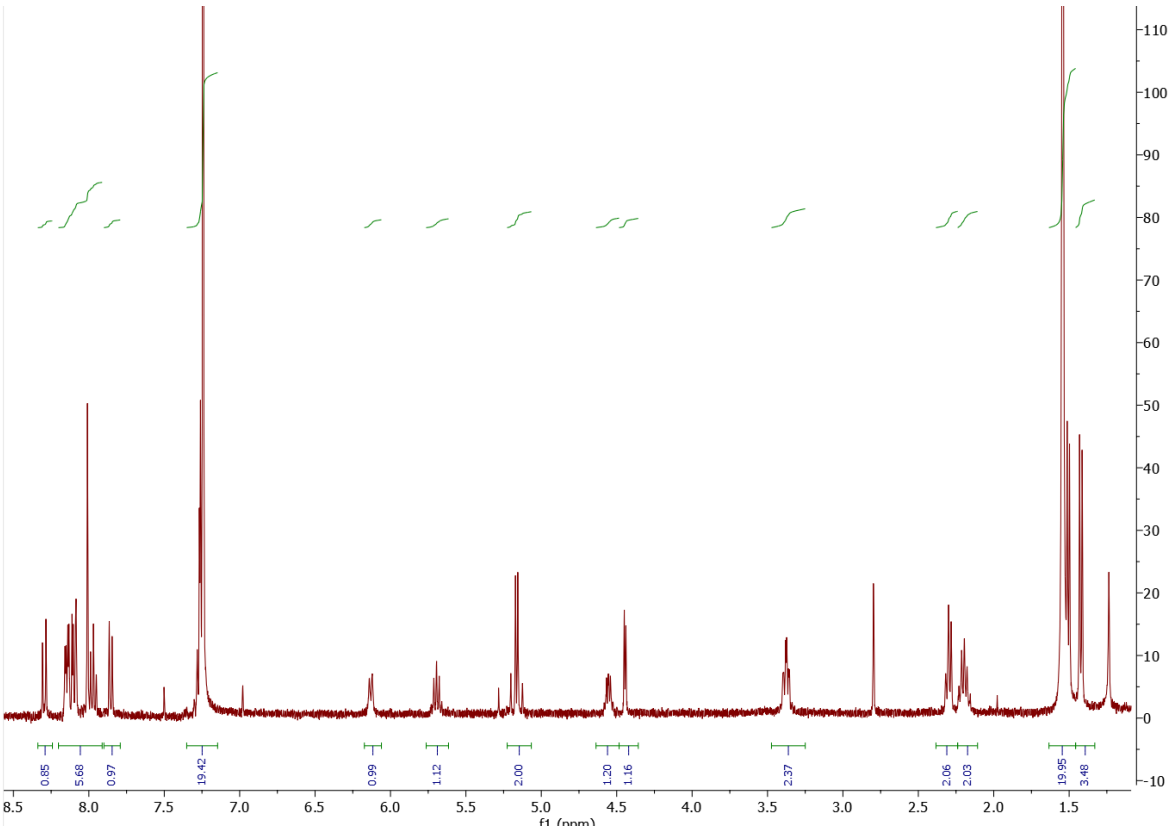
HPLC analysis of **dyad Inv10**



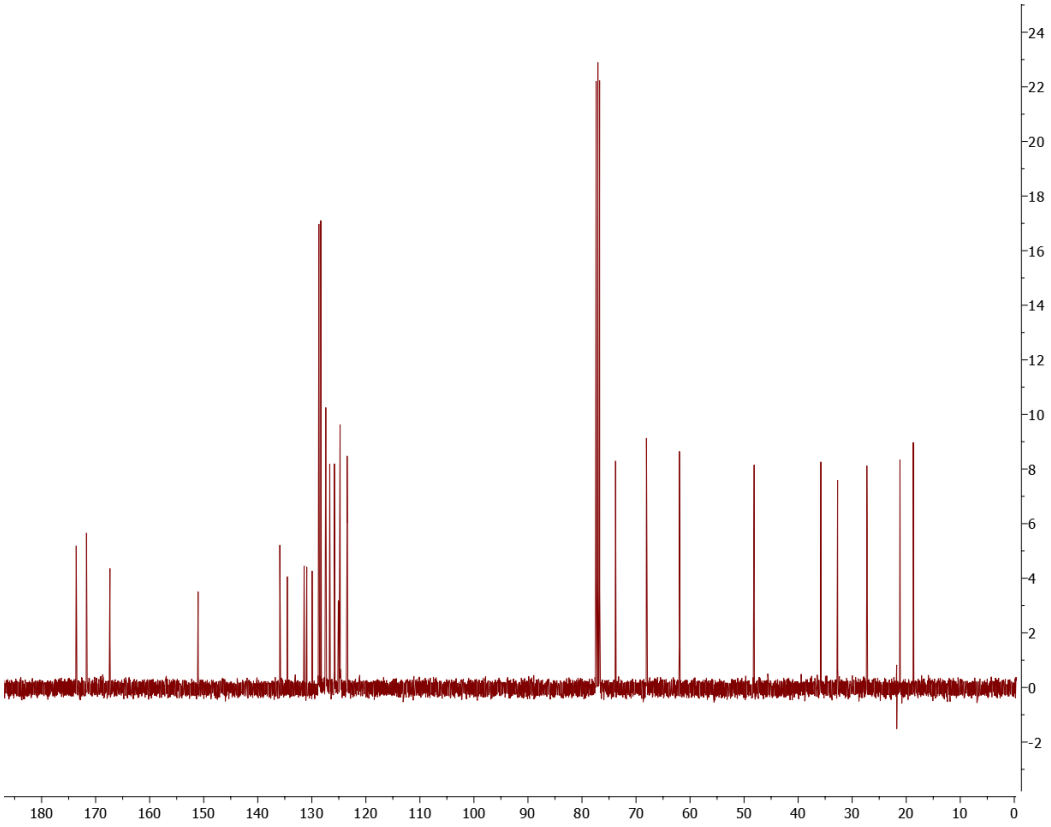
ATR-IR spectrum of **4-Py(CH_2)$_3$CO-L-Ala-D-Oxd-OBn Py-Inv' 6a**



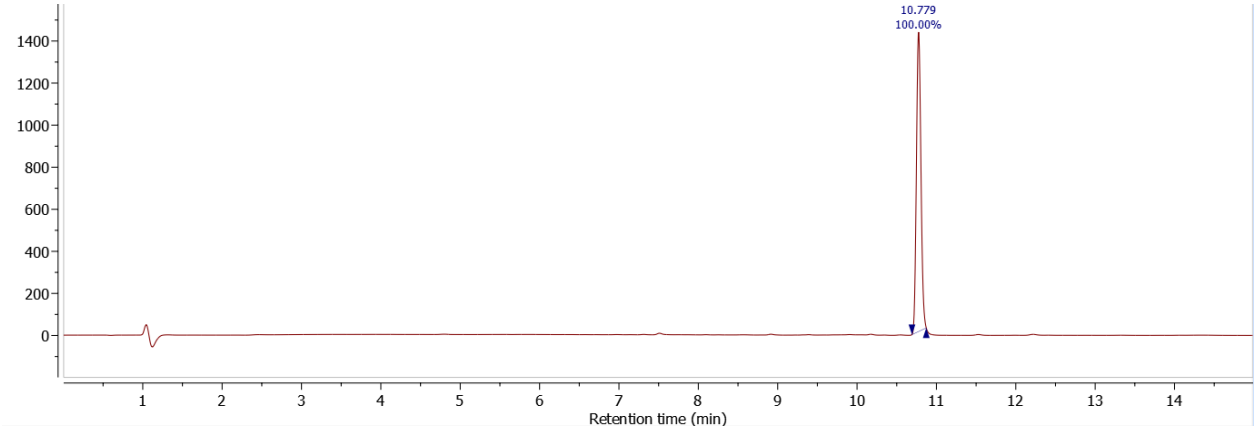
^{1}H NMR spectrum of **4-Py(CH_2)$_3$CO-L-Ala-D-Oxd-OBn Py-Inv' 6a**

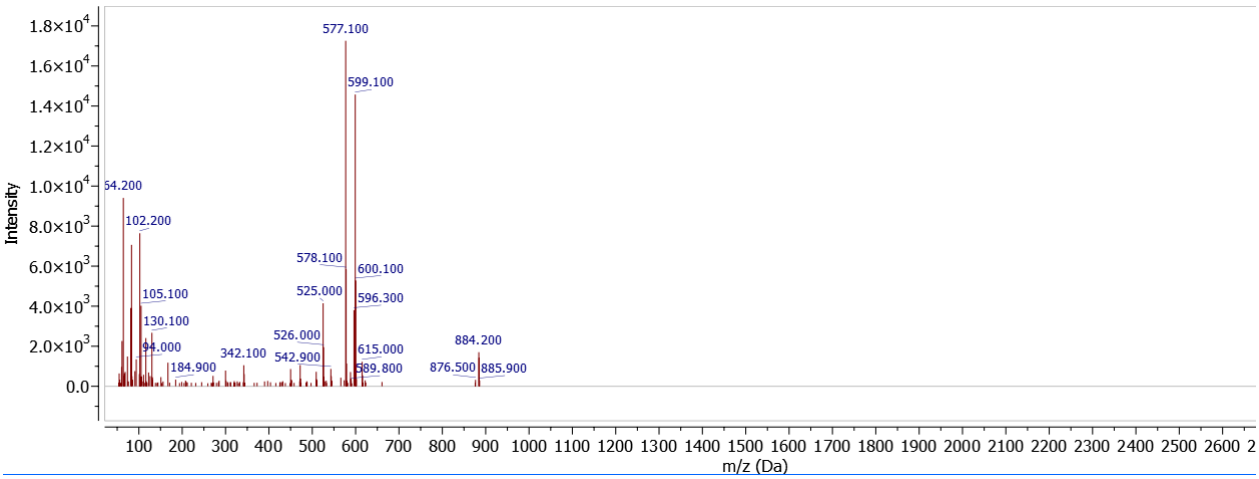


^{13}C NMR spectrum of **4-Py(CH$_2$)$_3$CO-L-Ala-D-Oxd-OBn Py-Inv' 6a**

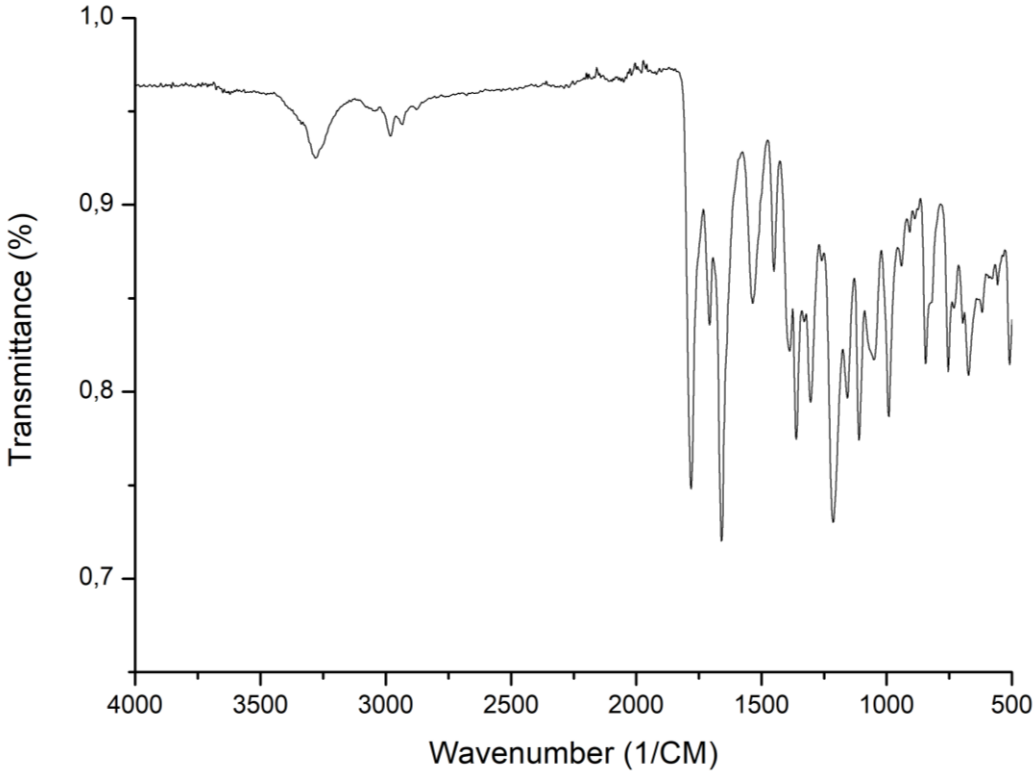


HPLC-MS analysis of **4-Py(CH_2)$_3$CO-L-Ala-D-Oxd-OBn Py-Inv' 6a**

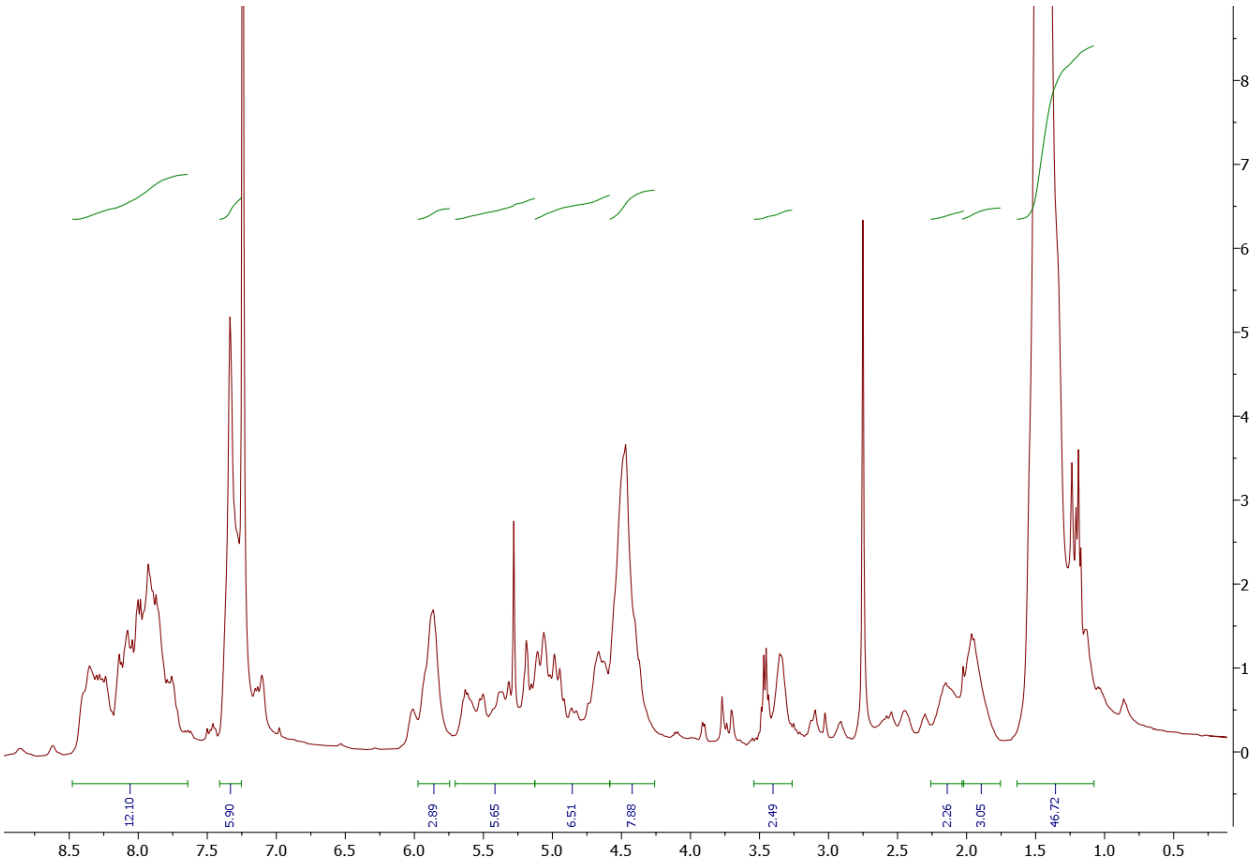




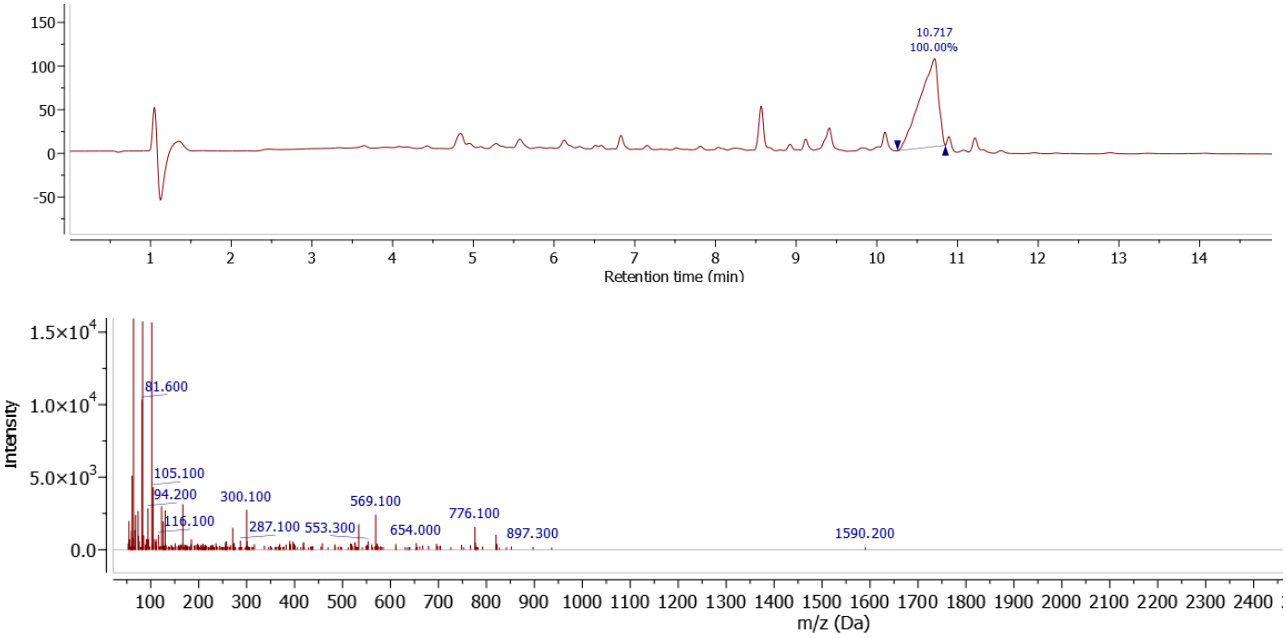
ATR-IR spectrum of **4-Py(CH$_2$)$_3$CO-(L-Ala-D-Oxd)$_6$-OBn 6b**



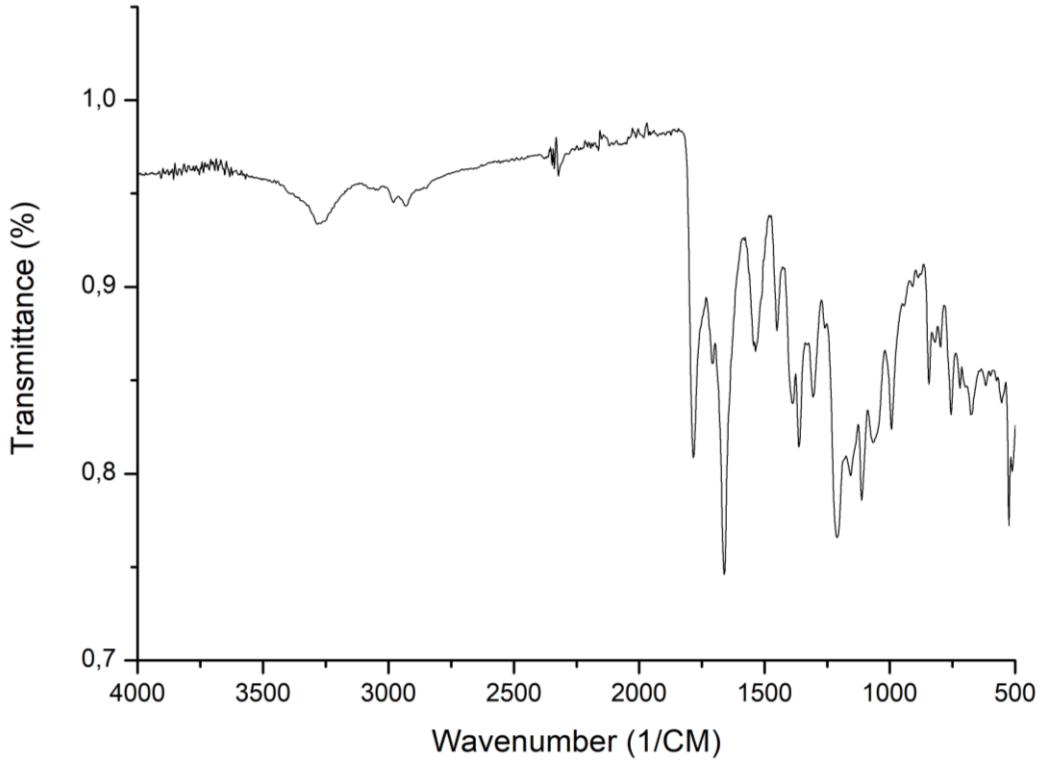
^{1}H NMR spectrum of **4-Py(CH$_2$)$_3$CO-(L-Ala-D-Oxd)$_6$-OBn 6b**



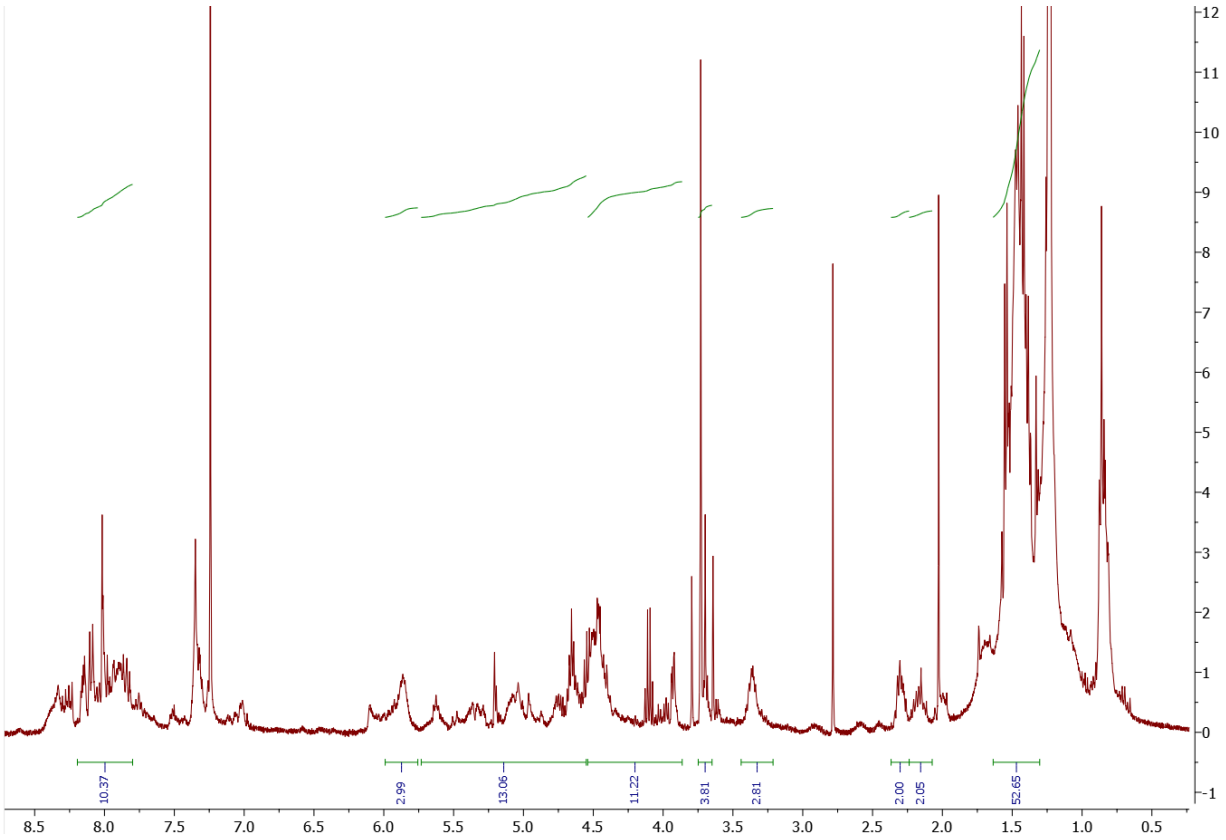
HPLC-MS analysis of **4-Py(CH$_2$)$_3$CO-(L-Ala-D-Oxd)$_6$-OBn 6b**



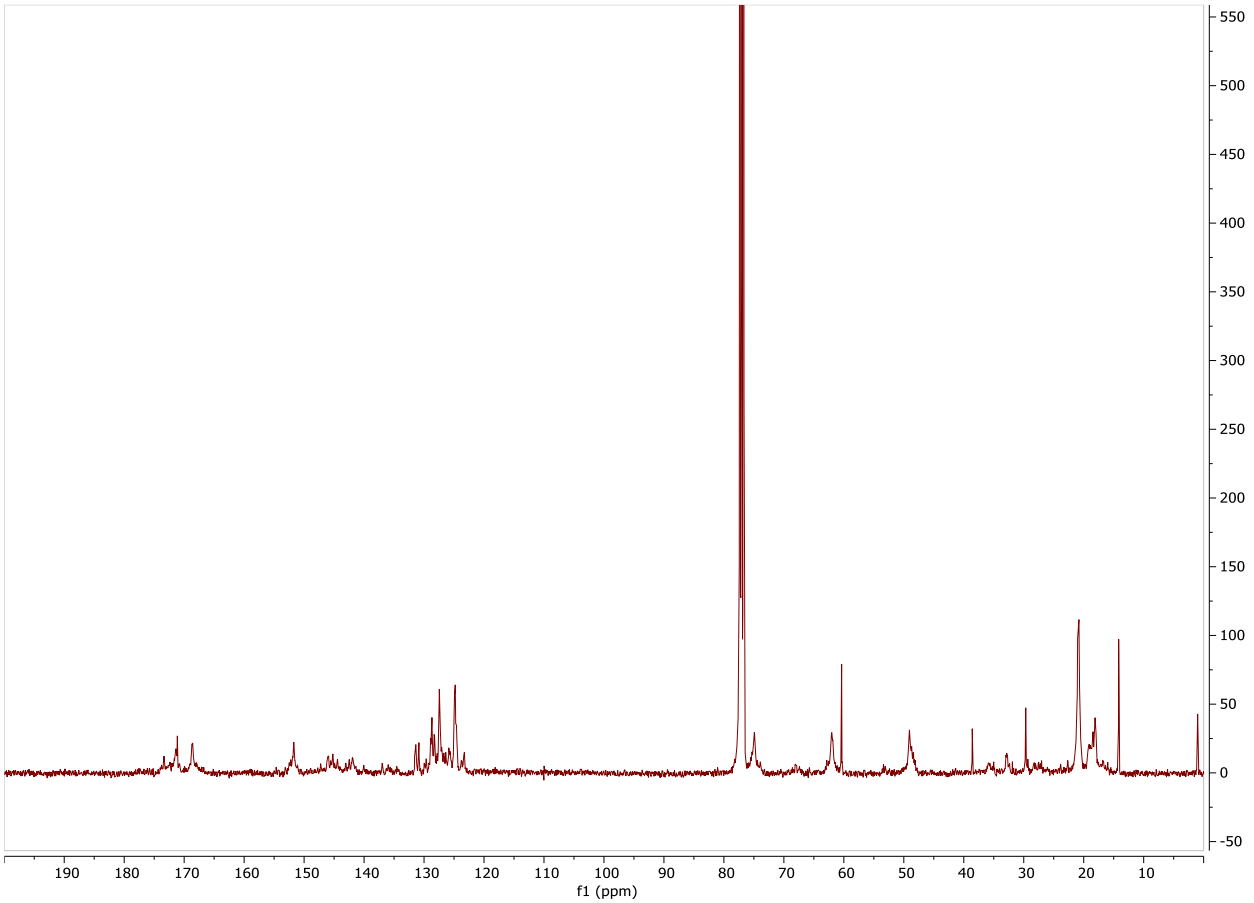
ATR-IR spectrum of **dyad Inv14**



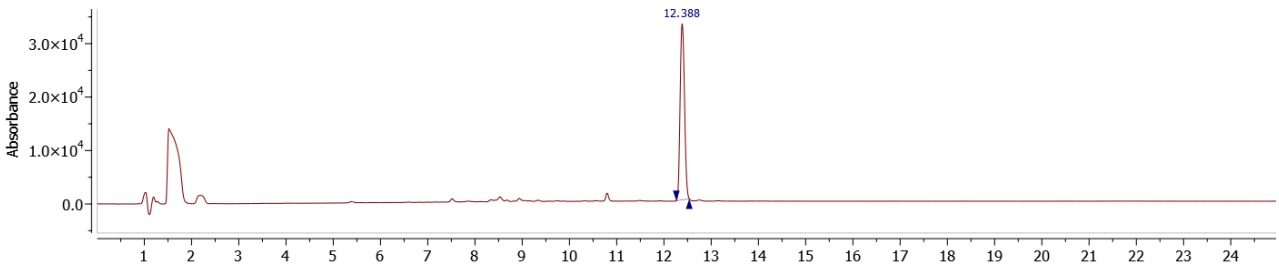
^{1}H NMR spectrum of **dyad Inv14**



^{13}C NMR spectrum of **dyad Inv14**



HPLC analysis of **dyad Inv14**



Electrochemical measurements

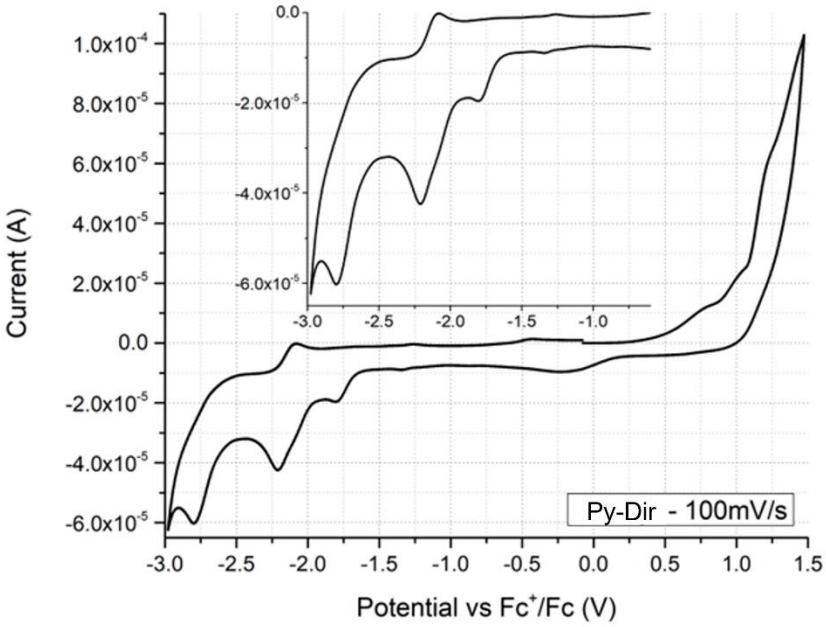


Figure S1. Cyclic Voltammetry of **Py-Dir** in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

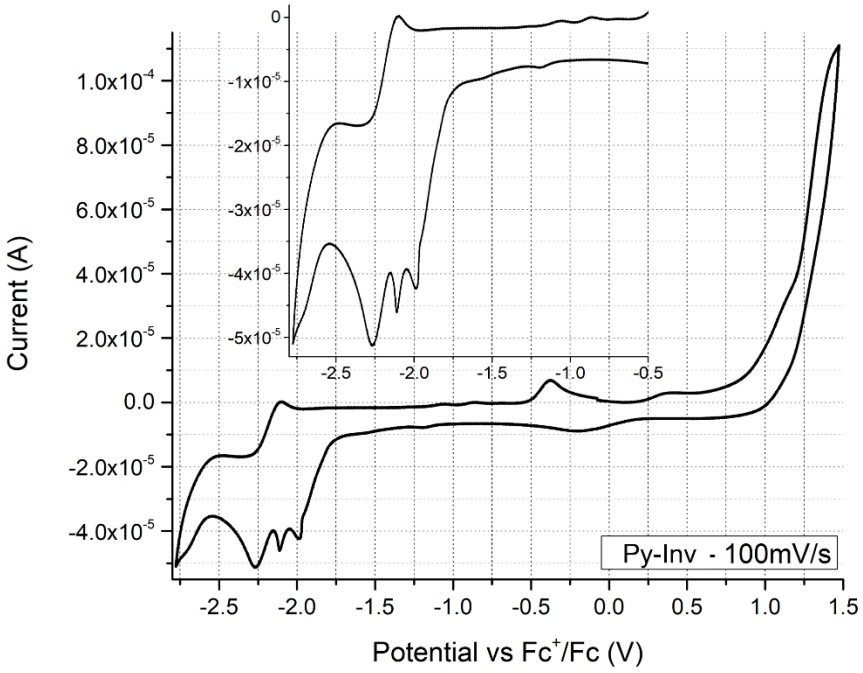


Figure S2. Cyclic Voltammetry of **Py-Inv** in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

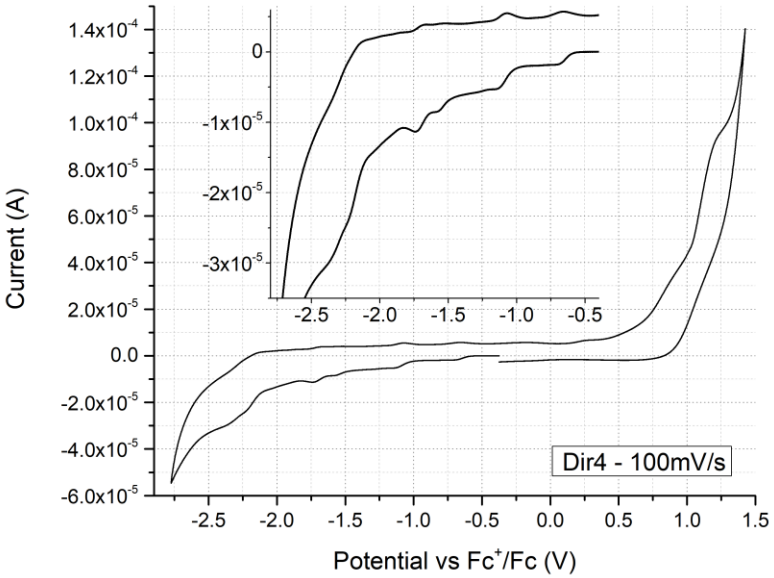


Figure S3. Cyclic Voltammetry of **Dir4** in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

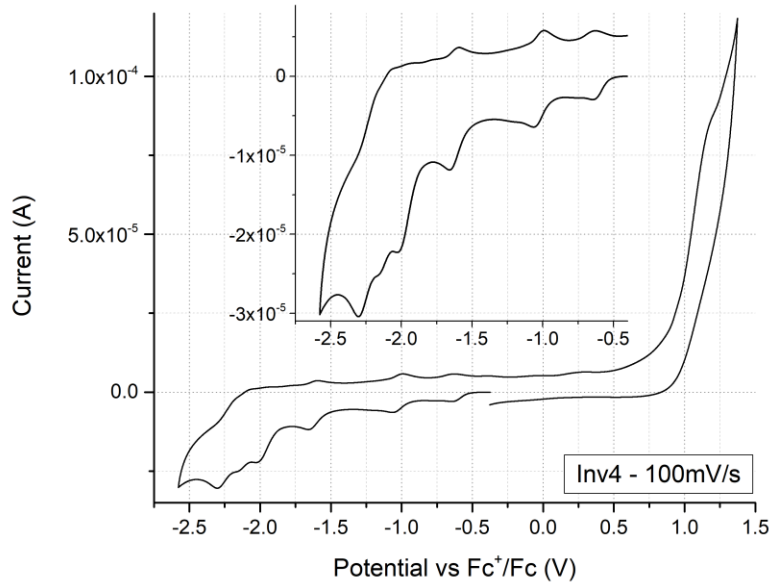


Figure S4. Cyclic Voltammetry of **Inv4** in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

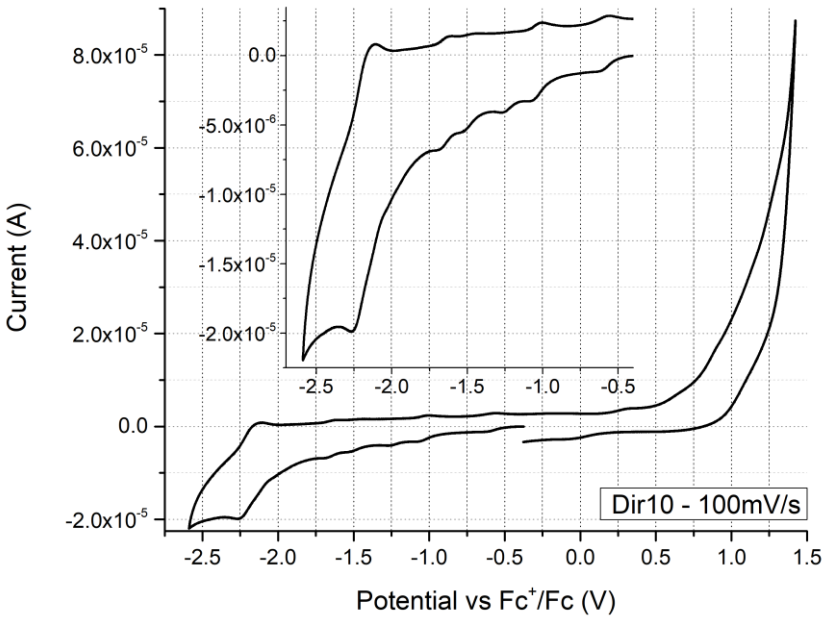


Figure S5. Cyclic Voltammetry of **Dir10** in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

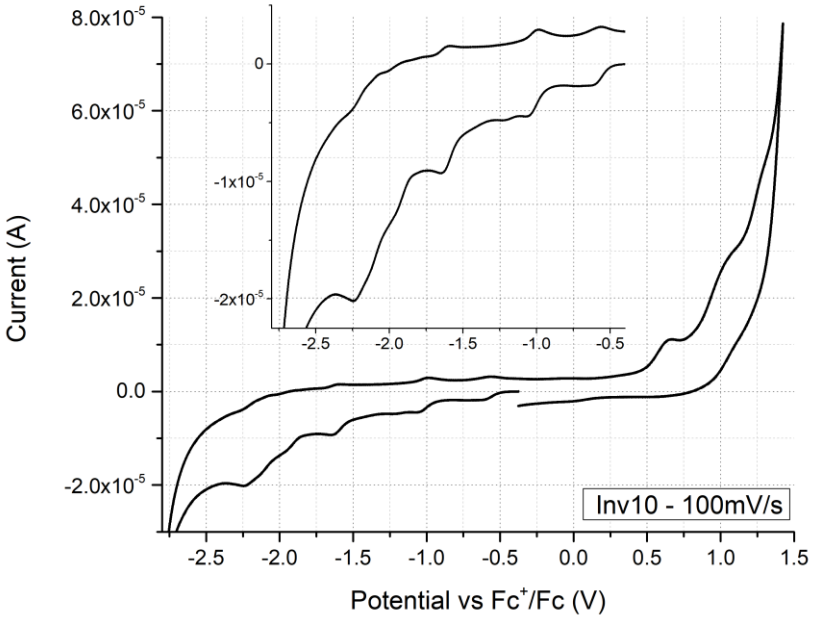


Figure S6. Cyclic Voltammetry of **Inv10** in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

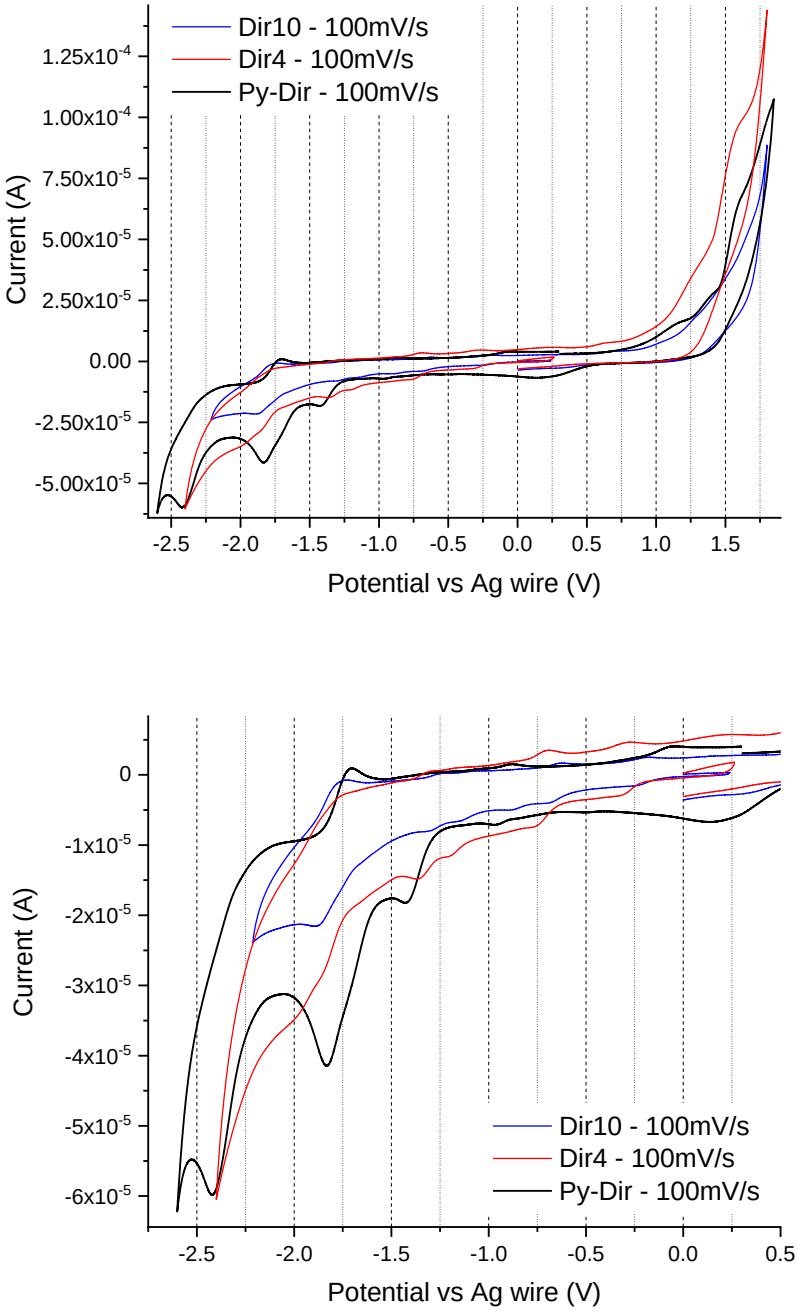


Figure S7. Cyclic Voltammetry of **Py-Dir** (black curve), **Dir4** (red curve), and **Dir10** (blue curve) in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

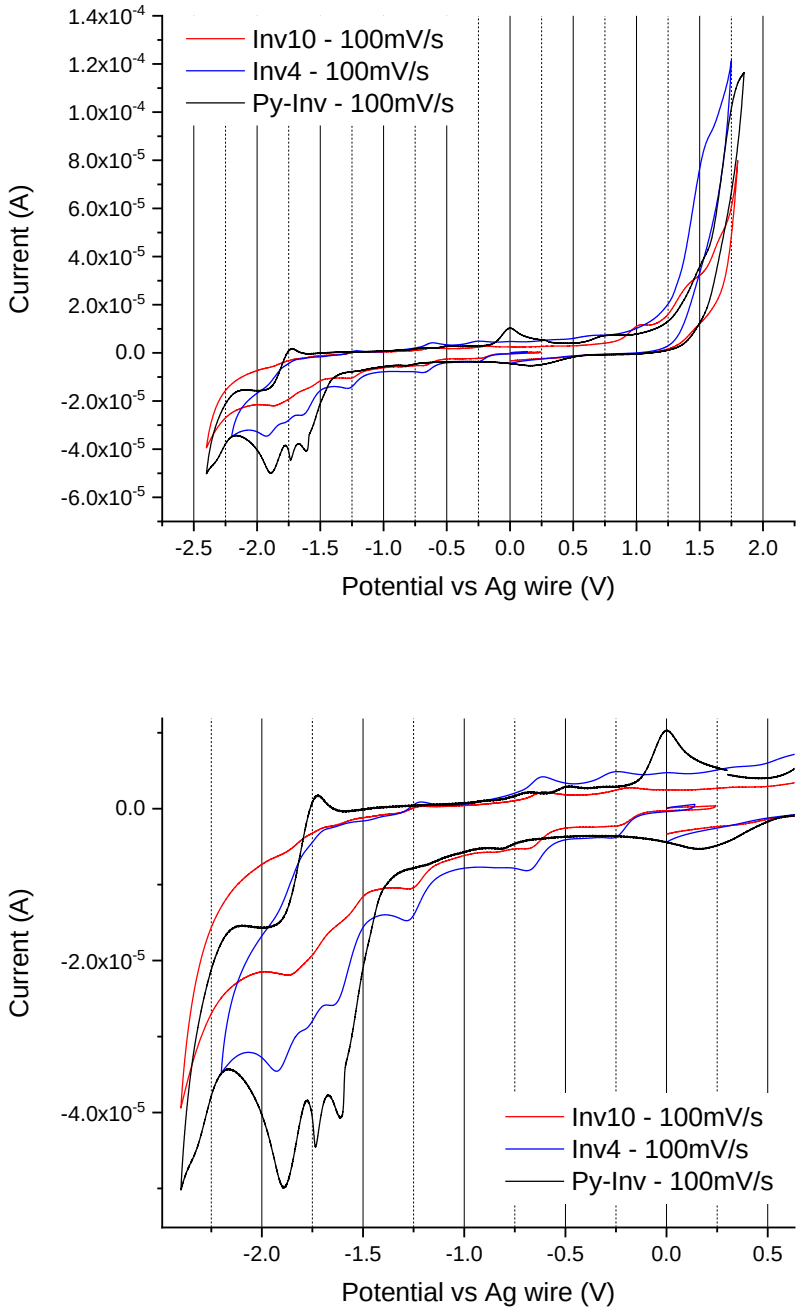


Figure S8. Cyclic Voltammetry of **Py-Inv** (black curve), **Inv4** (blue curve), and **Inv10** (red curve) in DMSO/toluene (1:1 v/v) / 0.1 M $TBABF_4$.

Photophysical measurements

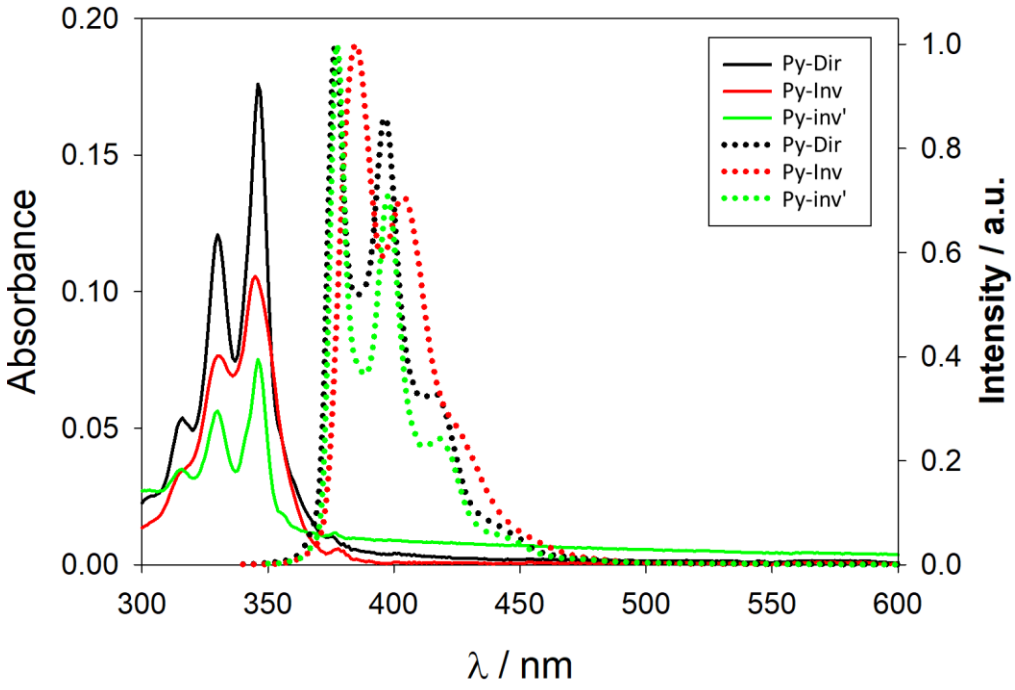


Figure S9. Absorption and emission spectra (λ_{exc} = 330 nm, normalized at maximum) of reference pyrenes.

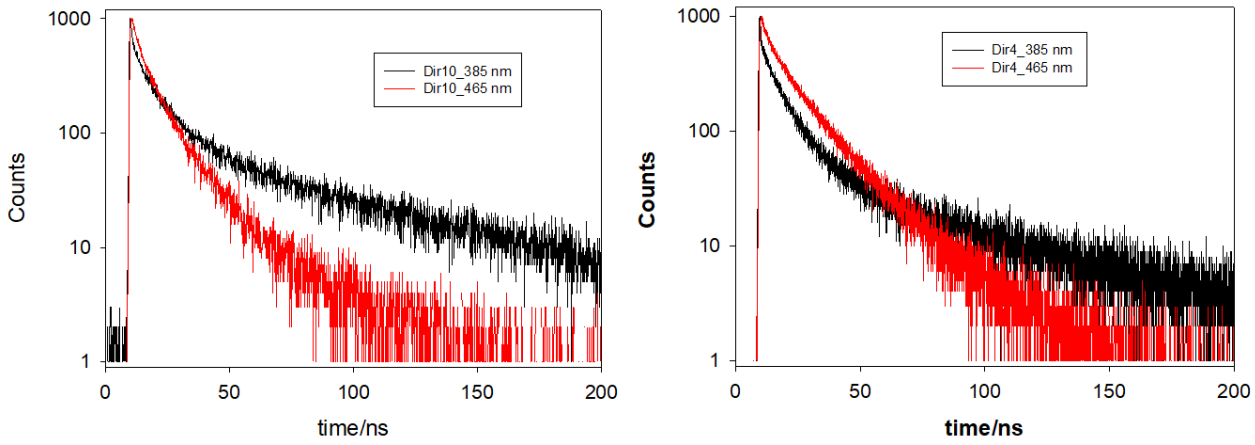


Figure S10. trPL decays of the dyads featuring aggregation (**Dir4** and **Dir10**) at 385 nm and 465 nm for monomer and excimer emissions, respectively. Fitting results are reported in the manuscript (Table 2).

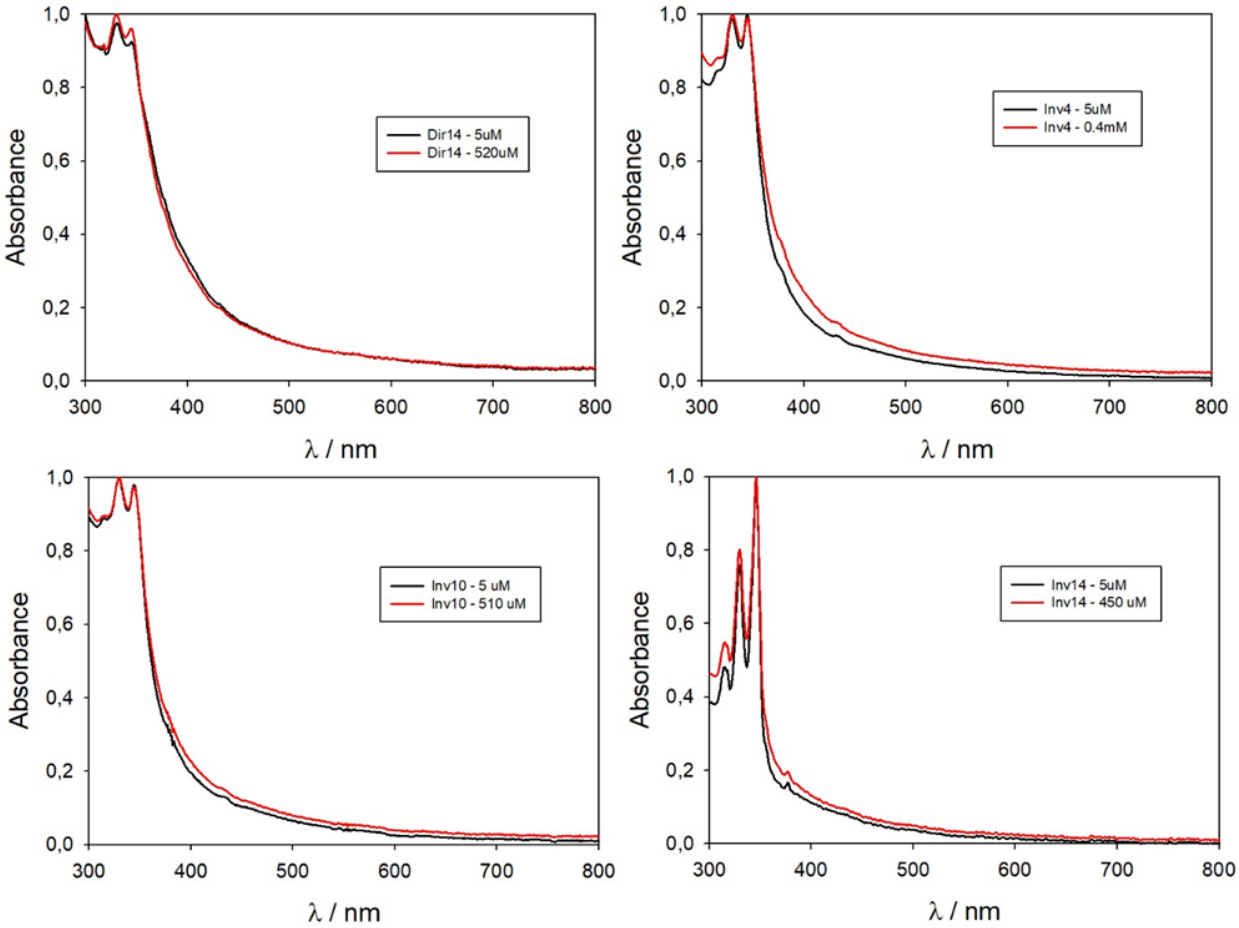


Figure S11. Absorption spectra of **Dir14**, **Inv4**, **Inv10**, and **Inv14** dyads at different concentrations. Black line = 5 μM, red line ≈ 0.5 mM (stock solution).

Time-resolved EPR measurements

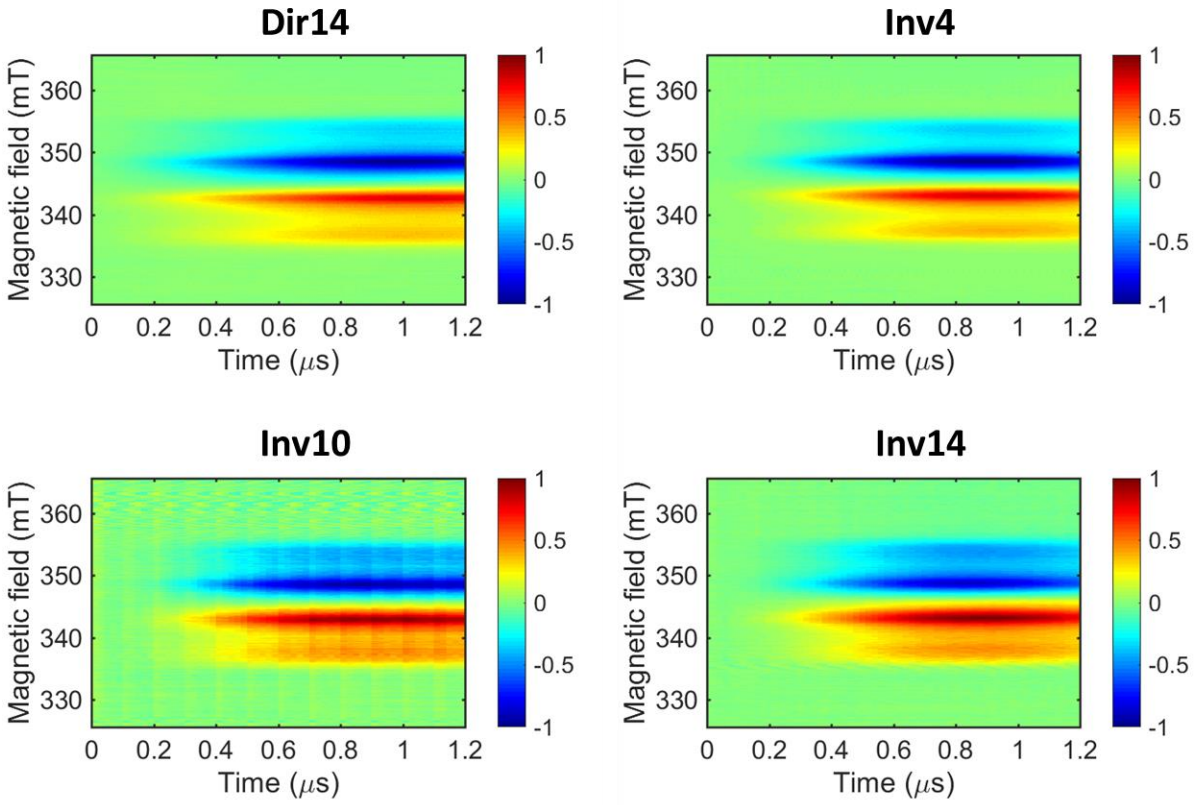


Figure S12. Normalised 2D experimental trEPR contour plots of **Dir14**, **Inv4**, **Inv10**, and **Inv14** acquired at 50 K after a 450 nm laser pulse (7 ns, 2 mJ). Colour legend: red = enhanced absorption, blue = emission, green = baseline.

g	*2.002*
[D E]/MHz	[-270 40]
LW/mT	1.6
[p_x p_y p_z]	[0.3 0.7 0.0]

Table S1. Best-fit parameters for the spectral simulations of the trEPR measurements reported in Figures 3b. The ZFS parameters of the triplet state are reported in units of MHz. From the ZFS parameters, we assigned the triplet to the C_{60} triplet populated *via* intersystem crossing in accordance with literature values.[3] Only Gaussian broadening was considered to avoid over-parametrization of the fitting; the full width at half maximum (LW) is reported in units of mT (for g = 2, 1 mT = 28 MHz).

Transient absorption

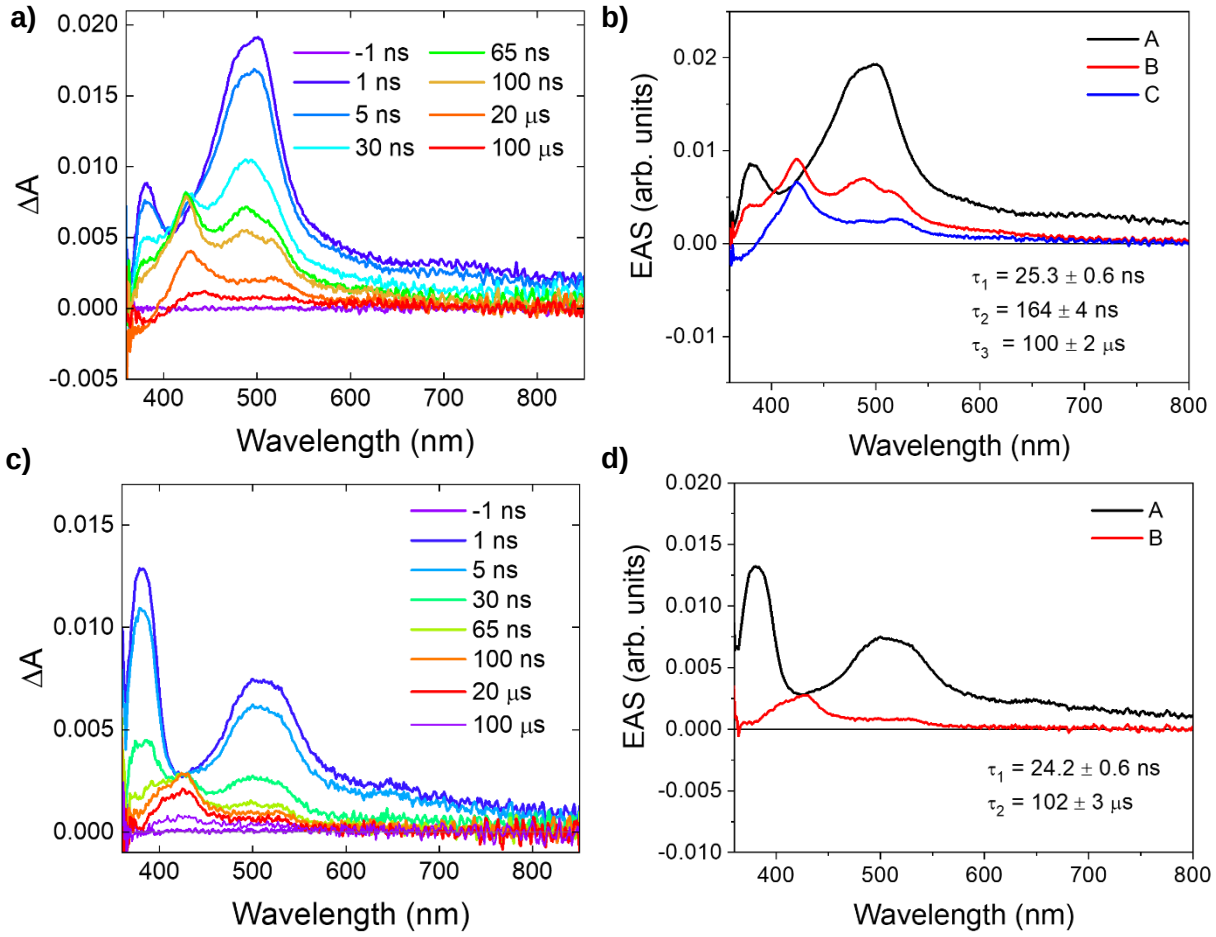


Figure S13. nsTA spectra in 1:1 v/v DMSO/toluene excited at 350 nm. (a) spectra of **Py-Dir**. (b) Evolution-associated spectra of **Py-Dir**. (c) spectra of **Py-Inv**. (d) Evolution-associated spectra of **Py-Inv**.

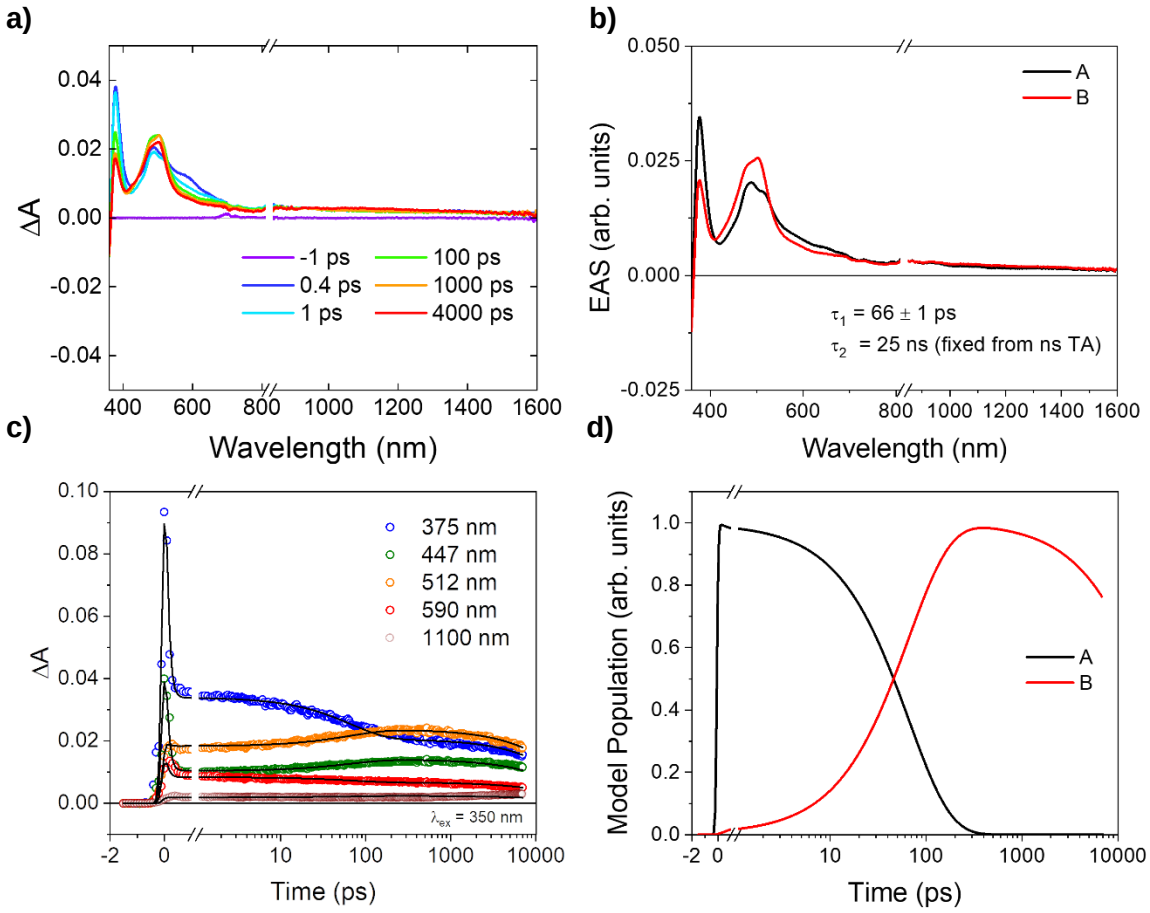


Figure S14. (a) fsTA spectra of **Py-Dir** in 1:1 v/v DMSO/toluene excited at 350 nm. (b) Evolution-associated spectra. (c) selected wavelength kinetic fits from global analysis, and (d) population dynamics of each species. The lifetime for Species B (τ_2) was fixed using the value from nanosecond TA.

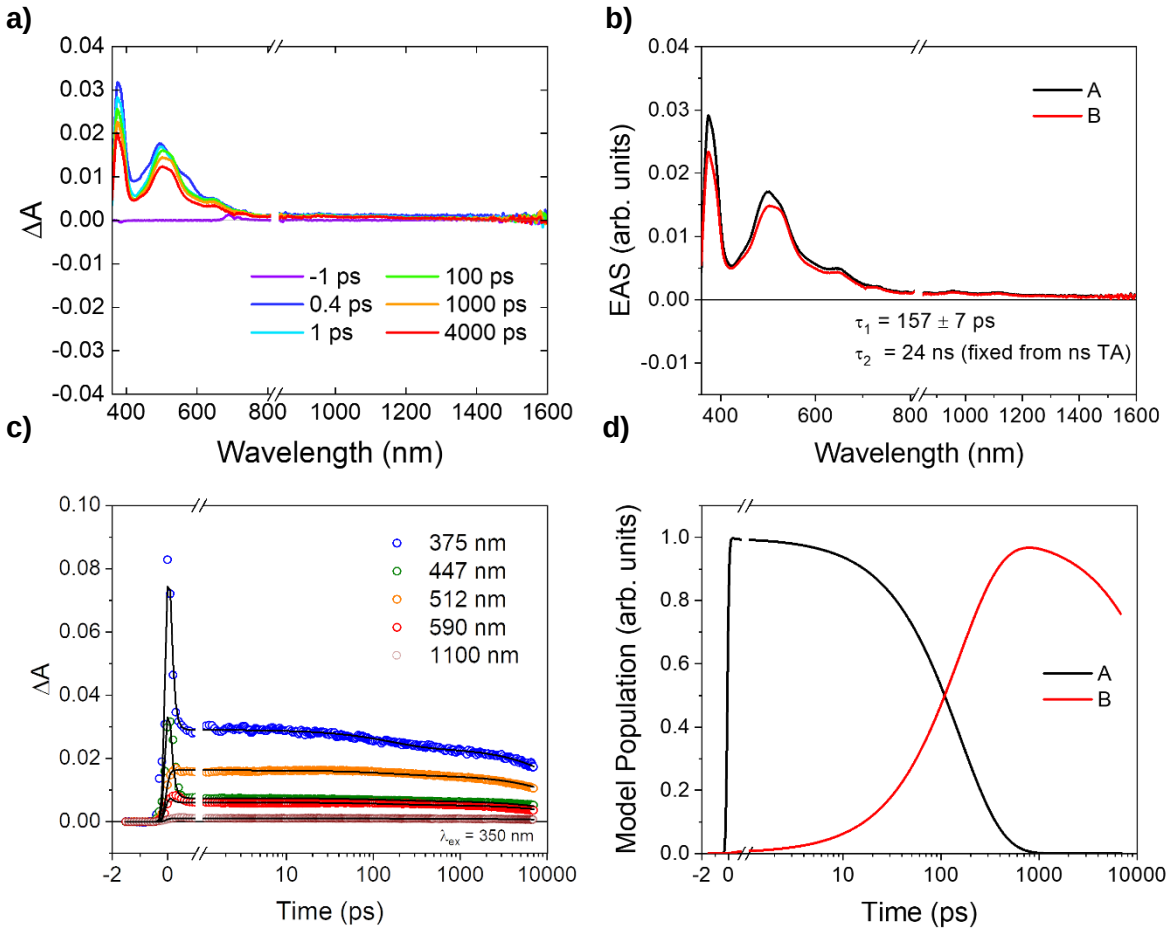


Figure S15. (a) fsTA spectra of **Py-Inv** in 1:1 v/v DMSO/toluene excited at 350 nm. (b) Evolution-associated spectra. (c) selected wavelength kinetic fits from global analysis, and (d) population dynamics of each species. The lifetime for Species B (τ_2) was fixed using the value from nanosecond TA.

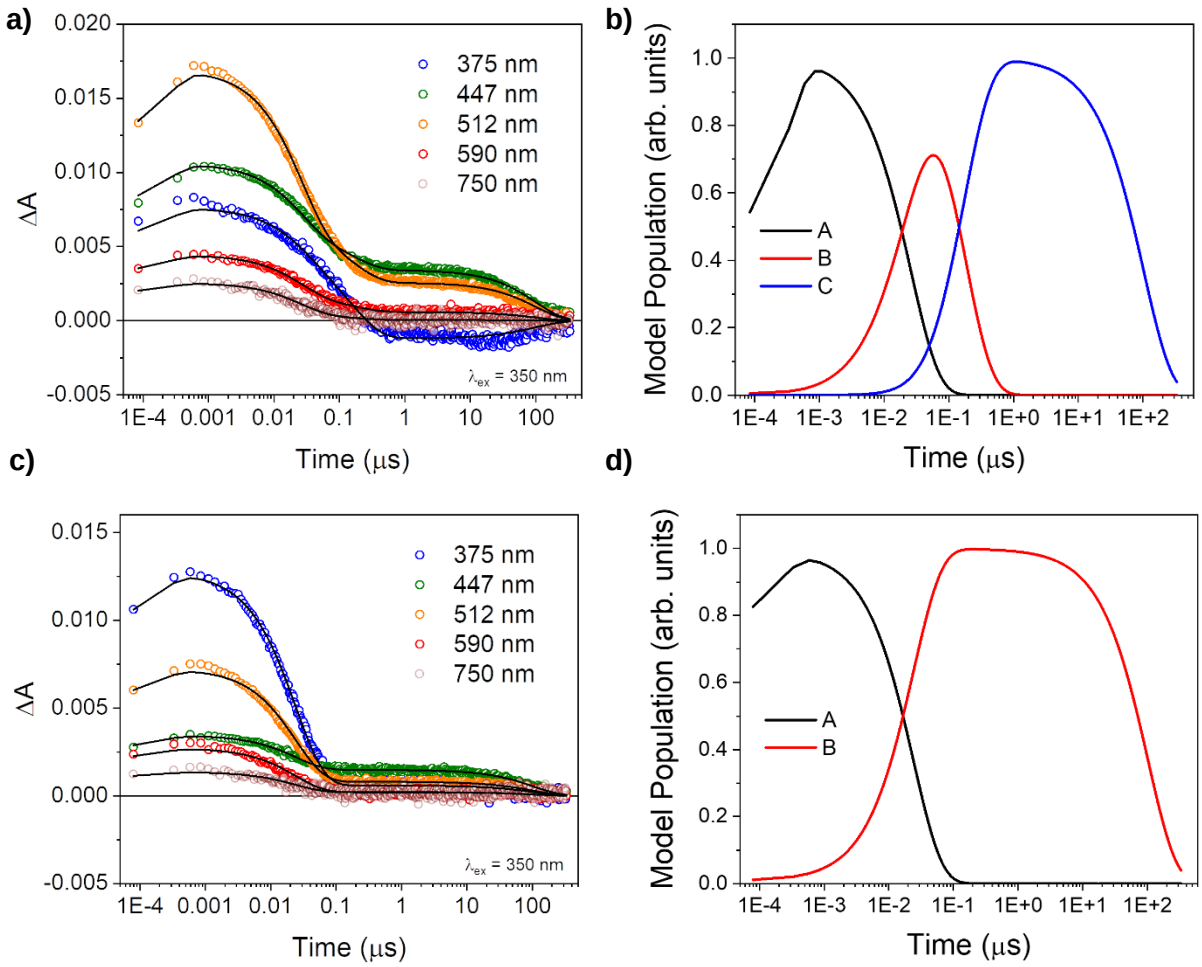


Figure S16. (a) Selected wavelength kinetic fits from global analysis of **Py-Dir** nsTA spectra. (b) population dynamics of each **Py-Dir** species. (a) Selected wavelength kinetic fits from global analysis of **Py-Inv** nsTA spectra. (b) population dynamics of each **Py-Inv** species.

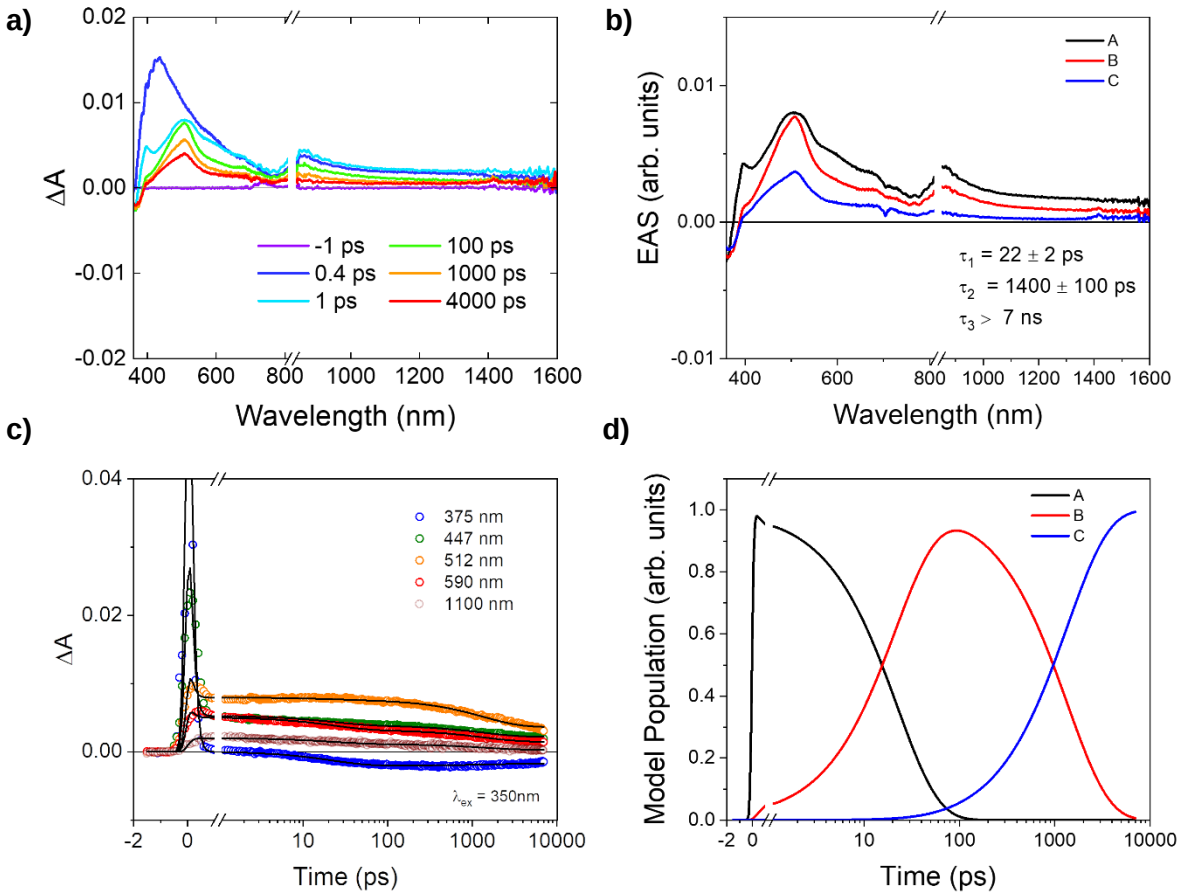


Figure S17. (a) fsTA spectra of **Dir4** in 1:1 v/v DMSO/toluene excited at 350 nm. (b) Evolution-associated spectra. (c) selected wavelength kinetic fits from global analysis, and (d) population dynamics of each species.

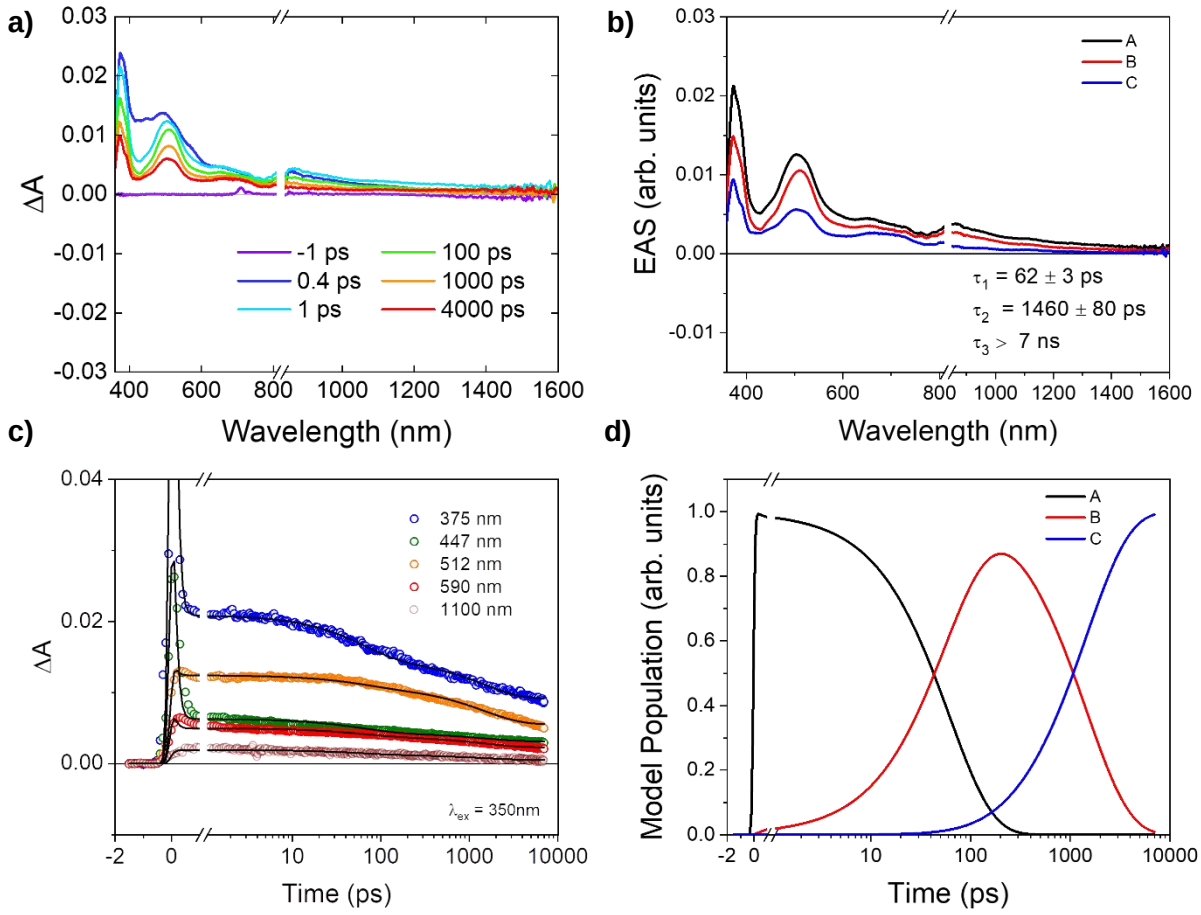


Figure S18. (a) fsTA spectra of **Inv4** in 1:1 v/v DMSO/toluene excited at 350 nm. (b) Evolution-associated spectra. (c) selected wavelength kinetic fits from global analysis, and (d) population dynamics of each species.

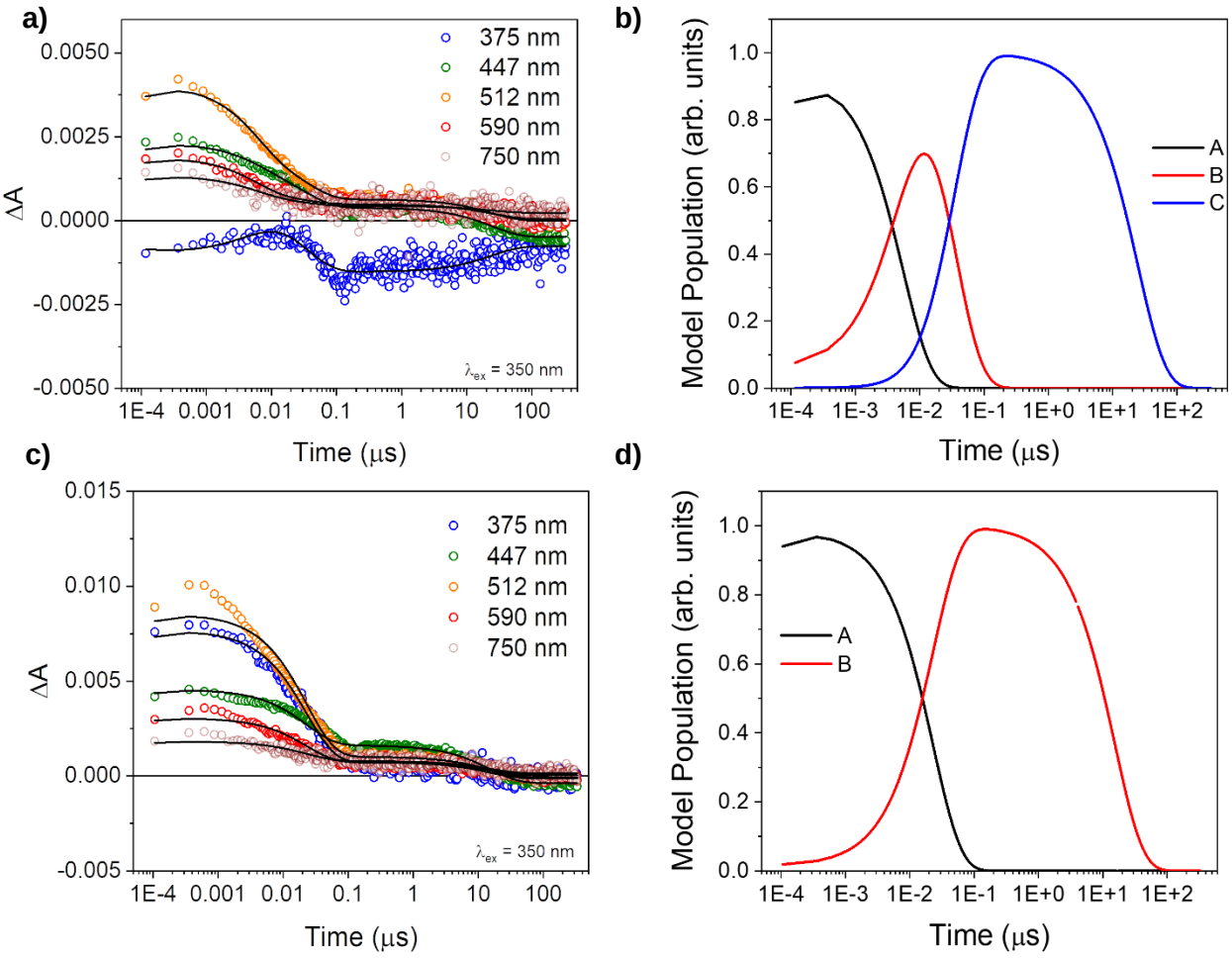


Figure S19. (a) Selected wavelength kinetic fits from global analysis of **Dir4** nsTA spectra. (b) population dynamics of each **Dir4** species. (c) Selected wavelength kinetic fits from global analysis of **Inv4** nsTA spectra. (d) population dynamics of each **Inv4** species.

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