Supplementary Information

Substitution pattern in ruthenium octa-*n*-butoxyphthalocyanine complexes influences their reactivity in N-H carbene insertions

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1. Materials and Methods

Unless otherwise noted, all commercially available compounds including ruthenium carbonyl (Sigma-Aldrich), o-dichlorobenzene (99%, Sigma-Aldrich), olefins and amines were obtained from Alfa Aesar or Sigma-Aldrich and were used without further purification. Benzonitrile was distilled under vacuum successively over P_2O_5 and over K_2CO_3, the pure solvent was stored under argon in the flask equipped with septum.

Ethyl diazoacetatate (EDA) containing ~ 13 wt% of dichloromethane was purchased from Sigma-Aldrich. Chloroform was distilled and kept over $NaHCO_3$ to remove acidic impurities. Solution of diazo acetonitrile in dichloroethane was prepared according to published protocol [1,2]. The diazo acetonitrile concentration was determined by ^{1}H NMR using standard (0.5 M DMSO solution in $CDCl_3$).

Octa-2,3,9,10,16,17,23,24-*n*-butoxyphthalocyaninato ruthenium (II) carbonyl complex **1β** was prepared by metalation with $Ru_3(CO)_{12}$ as previously described [3,4].

HRMS data were recorded were performed on a Bruker QTOF Impact II mass spectrometer. MALDI-TOF mass spectra were measured on a Bruker Daltonics Ultraflex mass spectrometer in positive ion mode using 2,5-dihydroxybenzoic acid (DHB) as a matrix. UV-visible absorption spectra (UV-Vis) were recorded on Thermo Evolution 210 or Agilent 8453 diade-array spectrophotometers in the 250−900 nm range in rectangular quartz with optical pathways of 10 mm. An FTIR Nexus (Nicolet) spectrophotometer with a micro-ATR accessory (Pike) was used to record IR spectra. ^{1}H and ^{19}F NMR spectra were acquired on a Bruker Avance HD (400 MHz) or AM 250 Bruker spectrometers at ambient temperature. Samples were prepared in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.), which was filtered through a layer of alumina prior to use. When recoding the NMR spectra of ruthenium phthalocyanines, the deuterated pyridine (10 µl per 0.6 ml $CDCl_3$) was added to NMR samples to prevent aggregation of the complexes. The NMR spectra were referenced to the solvent signals [5]. The reaction products were identified using the GC-MS technique (Hewlett Packard 5977B/7820A system; electron impact at 70 eV, He carrier gas, 30 m x 0.25 mm x 0.25 µm HP-5MS U1 capillary column).

Safety note

Handling of diazo compounds should be performed in a protected well-ventilated fume cupboard. General safety precautions when using solutions of diazo compounds should be followed. It should be pointed out that neat diazo acetonitrile was reported to be explosive [1]. Consequently, these compounds should be used either in diluted solution or be generated in situ according to the published safe protocols [1]. No accidents occurred handling of diazo compounds during this study. However, the reader should be aware of the potential explosiveness and carcinogenicity of these diazo compounds. The reactions reported in the present manuscript should be not carried out without proper safety precautions and risk assessment.

2. Synthesis and characterization of ruthenium phthalocyanine complexes

Octa-2,3,9,10,16,17,23,24-*n*-butoxyphthalocyaninatoruthenium(II) carbonyl, 1β

Ruthenium (II) carbonyl complex of octa-2,3,9,10,16,17,23,24-*n*-butoxyphthalocyanine 1β was prepared according to previously described procedure by reaction on corresponding metal-free phthalocyanine H_2[(β-BuO)$_8$Pc] with dodecacarbonyl triruthenium $Ru_3(CO)_{12}$ in o-dichlorobenzene under reflux [3,4].

3,6-*n*-dibutoxyphthalonitrile

3,6-dihydroxyphthalonitrile (3.14 g, 19.6 mmol), KI (6.51 g, 39.2 mmol), K_2CO_3 (16.22 g, 117.5 mmol) were placed into a 100 ml double-neck flask equipped with the reflux condenser under argon. After addition of DMF (20 mL) and *n*-butylbromide (8.056 g, 6.31 ml, 58.8 mmol) the resulting suspension was heated at 80ºC under argon for 23 h. Then, the reaction mixture was poured in 100 mL of water. The brown precipitate was separated by filtration, washed with 30 mL of water and dried. The crude product was dissolved in 500 mL of $CHCl_3$/MeOH mixture and one spoon of silica was added. After evaporation of the solvents, the obtained solid was transferred onto column packed with SiO_2 in hexane/$CHCl_3$ (1:1 vol.) mixture. Gradient elution with hexane/$CHCl_3$ (50 → 100 vol. %) and chloroform/MeOH (0 → 1 vol. %) followed by the solvent evaporation afforded the pink solid. The pure target phthalonitrile was obtained by recrystallization from EtOH (75 mL) as white fluffy crystals (4.66 g, 87%). The ^{1}H NMR spectrum was in agreement with the previously reported data [6].

- ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm): 7.14 (s, 2H), 4.06 (t, J = 6.4 Hz, 4H), 1.85 – 1.78 (m, 4H), 1.53 (h, J = 7.4 Hz, 4H), 0.98 (t, J = 7.4 Hz, 6H).

Octa-1,4,8,11,15,18,22,25-*n*-butoxyphthalocyanine, H_2[(α-BuO)$_8$Pc]

3,6-di-*n*-butoxyphthalonitrile (824 mg, 3.0 mmol) and granulated lithium (84.7 mg, 12.1 mmol) were placed into a 50 mL flask equipped with the reflux condenser. Dry *n*-butanol (10 mL) was added to the flask and the suspension was degassed by three pumping - argon flushing cycles. The flask was placed into metal bath preheated to 130ºC. After 5 min lithium began to dissolve and within 10 min the solution changed the colour from transparent to dark-green. The reaction mixture was heated at 130° for 15 h. Then, the reaction mixture was cooled to 60ºC and 10 mL of glacial acetic acid was added. According to UV-Vis spectra, the demetallation was completed within 25 min. The reaction mixture was neutralized with an aqueous $NaHCO_3$ solution, washed with water (60 mL) and extracted with chloroform (3 x 50 mL). To combined organic fractions one spoon of silica was added and the solvent was carefully evaporated. The obtained solid was transferred onto column packed with SiO_2 in hexane/$CHCl_3$ (1:1 vol.) mixture and the product was obtained by gradient elution with hexane/$CHCl_3$ (50 → 100 vol. %). Further purification by size-exclusion chromatography on Bio-Beads SX-1 ($CHCl_3$+2.5 vol.% MeOH) afforded the metal-free phthalocyanine H_2[(α-BuO)$_8$Pc] (565 mg, 68%) as a dark-green solid.

The spectral parameters were in agreement with the previously reported data [7]

- UV-Vis, $CHCl_3$, λ_{max}, nm ($A_{normalized}$): 774 (1.00), 752 (0.90), 709 (0.27), 680 (0.24), 331 (0.45).
- MALDI TOF MS, m/z: found 1090.6 – $[M+H]^+$, calculated for $[M]^+$, $C_{64}H_{82}N_8O_8^+$ – 1089.6
- ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm): 7.59 (s, 8H, H_{Pc}), 4.86-4.84 (m, 16H, α-CH_2), 2.24 – 2.19 (m, 16H, β-CH_2), 1.69 – 1.60 (m, 16H, γ-CH_2), 1.09-1.06 (t, J = 7.4 Hz, 24H), 0.25 (s, 2H, N-H).

Note 1. The choice of the solvent is crucial: when *n*-pentanol was used, a nucleophilic aromatic substitution of the butoxy groups occurred. The product isolated after chromatographic purification contained phthalocyanines with various amount of butoxy and pentoxy groups.

Note 2. Dissolving lithium at lower temperature followed by the reflux of the reaction mixture results in a lower yield of the target phthalocyanine.

Octa-1,4,8,11,15,18,22,25-*n*-butoxyphthalocyaninatoruthenium(II) carbonyl, 1α

The mixture of phthalocyanine H_2[α-$(BuO)_8$Pc] (49.3 mg, 45.2 μmol) and $Ru_3(CO)_{12}$ (43.3 mg, 67.8 μmol) was dissolved in dry benzonitrile (10 mL) in the two-neck flask, equipped with the reflux condenser. The mixture was degassed by three-times pumping and flushing with argon on the Schlenk line. Then, the flask was immersed into the metal bath preheated to 190 °C. The reaction mixture was refluxed under argon for 30 min, until the Q-band of the starting phthalocyanine (773 nm) vanished in the UV-Vis spectra of the reaction mixture samples and the Q-band of the metal complexes (717 nm) appeared. The reaction mixture was cooled to ambient temperature and the solvent was removed under reduced pressure (10 mmHg, 95-98 °C). The reaction mixture was transferred onto the chromatographic column packed with SiO_2 in hexane/$CHCl_3$ (1:1 vol.) mixture. Gradient elution with hexane/$CHCl_3$ (50 → 100 vol. %) and chloroform/MeOH (0 → 3 vol. %) gave a blue band containing the target complex. Further purification by size exclusion chromatography on Bio-Beads SX-1 gel in $CHCl_3$ containing 2.5 vol.% MeOH afforded to the pure complex **1α** (40.3 mg, 73%) as dark-green solid.

Note 1. The purity of benzonitrile is crucial for successful metalation. When benzonitrile is stored for long time, some impurities (presumably, benzamide) can be formed that suppresses the complex formation. Thus, benzonitrile was distilled successively over P_2O_5 and K_2CO_3 and stored under argon.

- HRMS (ESI), m/z: found 1219.510 – $[M+H]^+$, calculated for $[C_{65}H_{81}N_8O_9Ru]^+$ – 1219.519.
- MALDI TOF MS, m/z: found 2383.6 – $[M\text{-}CO]_2^+$, calculated for $[C_{128}H_{160}N_{16}O_{16}Ru_2]H^+$ – 2382.0; found 1192.3 – $[M\text{-}CO]^+$, calculated for $[C_{64}H_{80}N_8O_8Ru]H^+$ – 1191.5
- UV-Vis in CH_2Cl_2, λ_{max}, nm (lgε): 709 (5.20), 638 (4.58), 299 (4.78).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 8H, HPc), 4.90-4.81 (br m, 16H, α-CH_2), 2.34 – 2.27 (m, 16H, β-CH_2), 1.69 – 1.64 (m, 16H, γ-CH_2), 1.14-1.11 (t, J = 7.4 Hz, 24H).
- FTIR, ν cm^{-1}: 3348, 3252, 2956, 2871, 1947 - $\nu^{(CO)}$, 1596, 1498, 1378, 1257, 1205, 1111, 1062, 961, 914, 810, 718.

References

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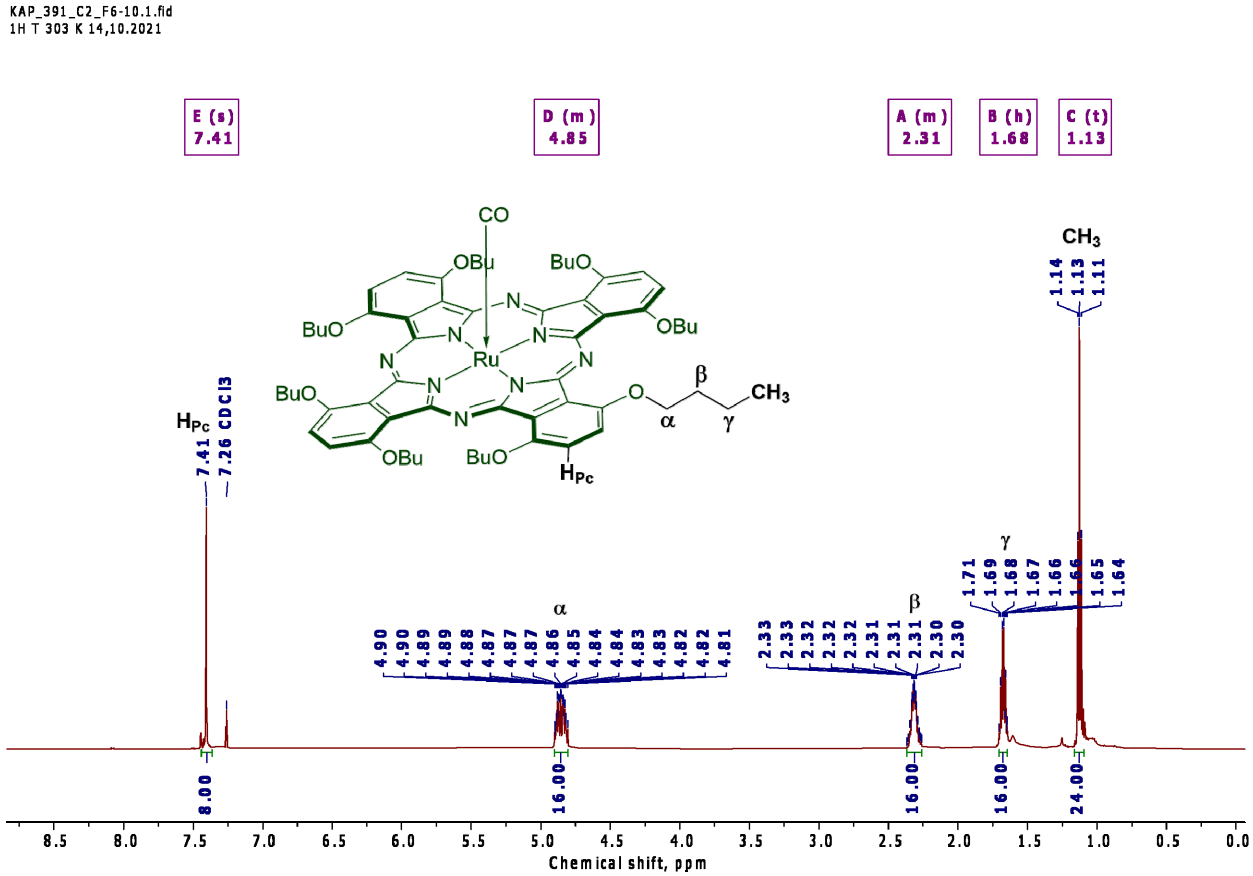


Figure S1. ^{1}H NMR spectrum of non-peripherally substituted **1α**.

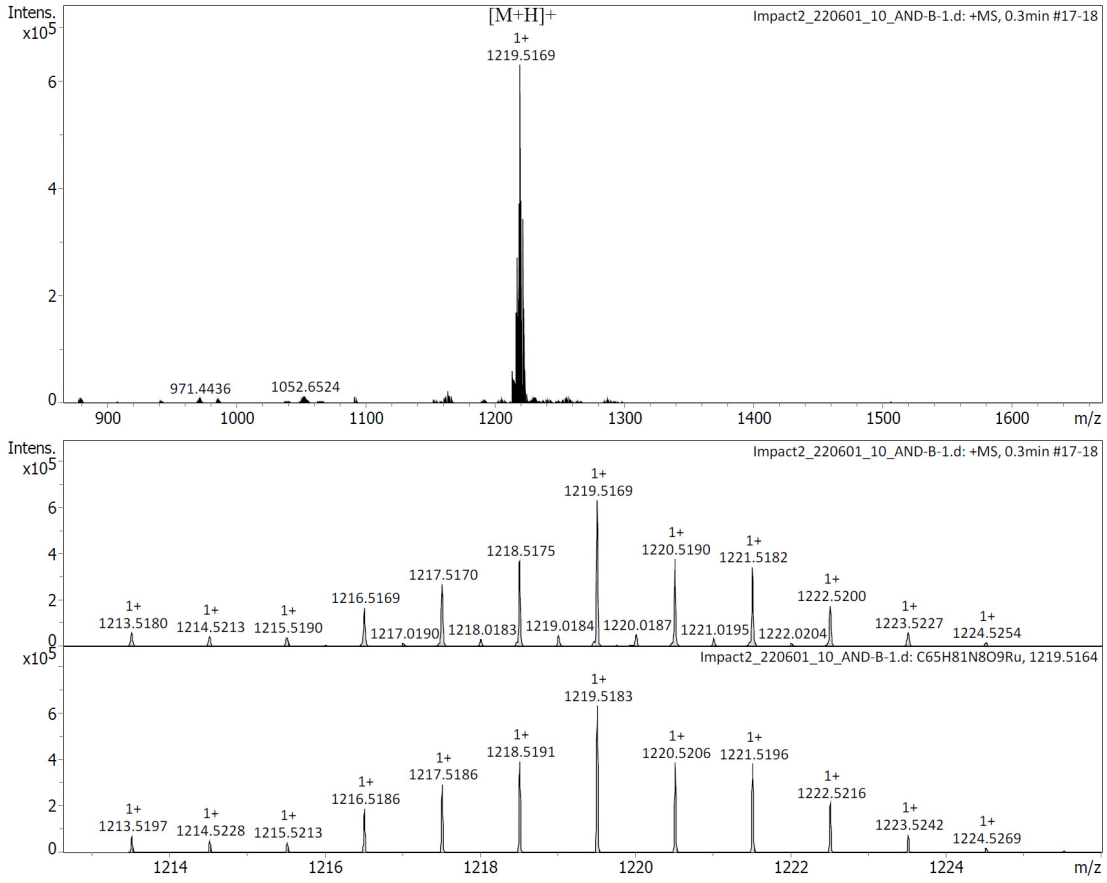


Figure S2. HRMS (ESI) spectrum of non-peripherally substituted **1α**.

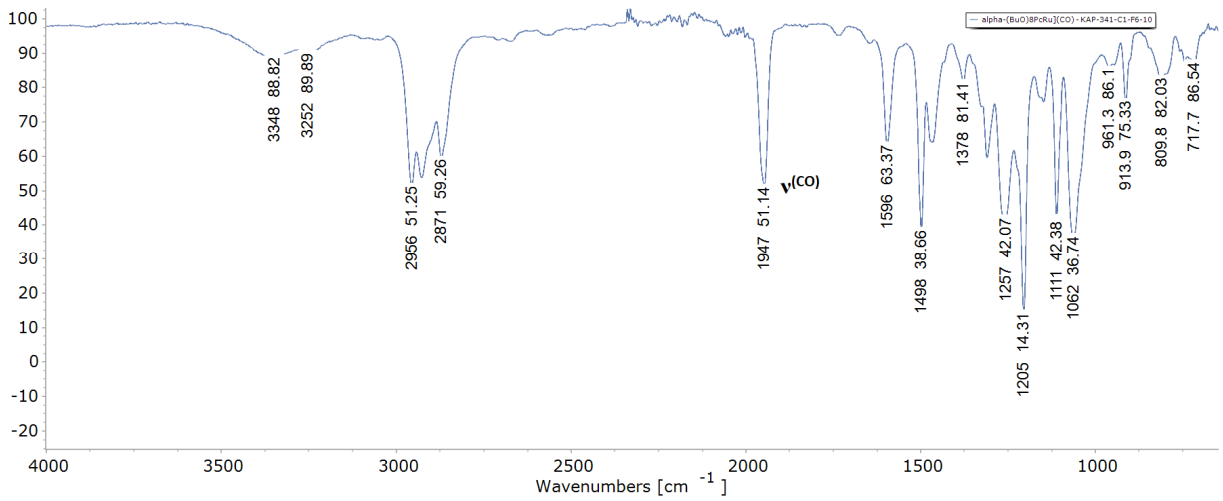


Figure S3. IR spectrum of non-peripherally substituted complex **1α**.

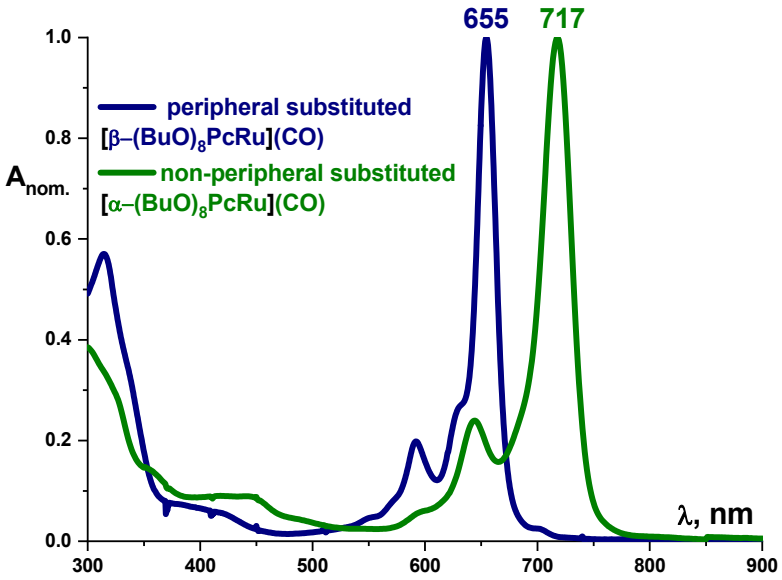


Figure S4. UV spectra of peripherally and non-peripherally substituted ruthenium complexes **1β** and **1α** in chloroform.

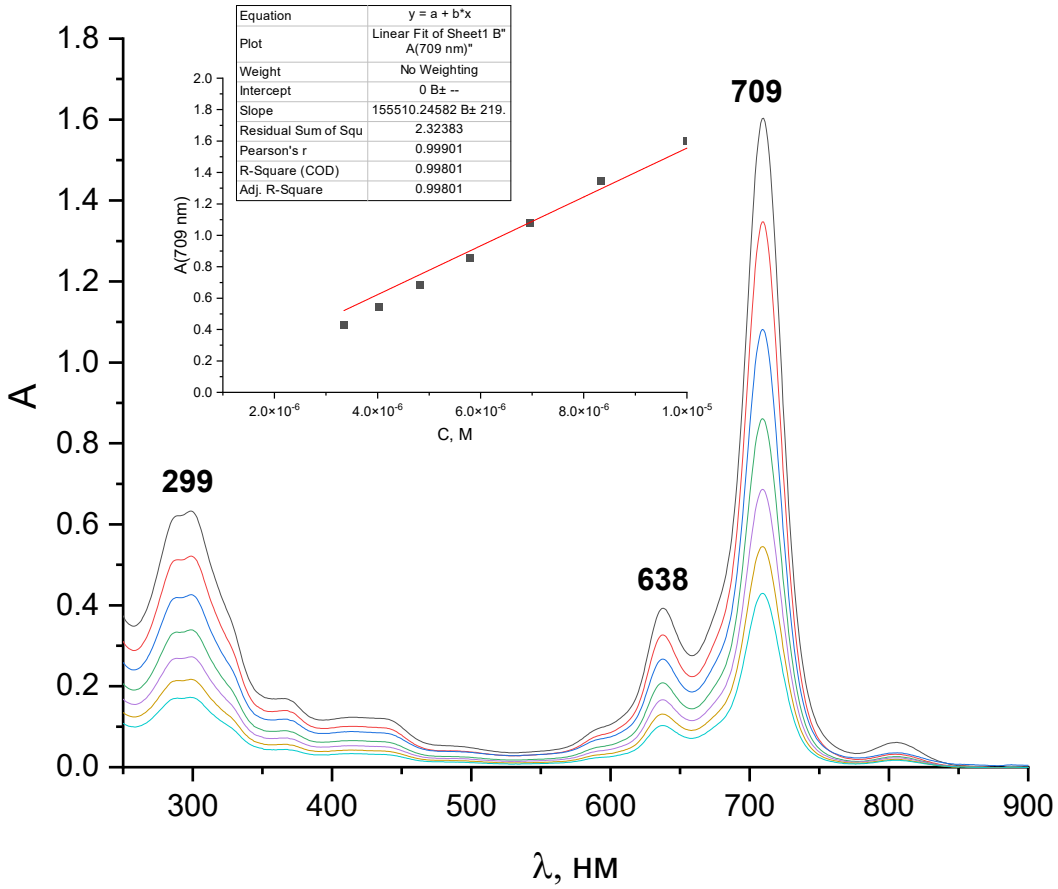


Figure S5. Concentration-dependent UV-Vis spectra of complex **1α** in CH_2Cl_2.

3. Catalytic procedures

Carbene N-H insertion of amines in the presence of non-peripherally substituted ruthenium complex 1α

EDA (127 μL, 1.05 mmol, 2.1 equiv.) was added to a solution of amine (1 M, 0.5 mmol, 1 equiv.) and **1α** (0.5 mM, $7.5 \cdot 10^{-4}$ mmol, 0.15 mol%) in 0.5 mL of dichloromethane under air at 40°C. The reaction mixture was stirred for 2-4 h. The reaction products were analyzed by GC-MS and ^{1}H NMR ($CDCl_3$) techniques. Careful analyses of ^{1}H NMR and ^{19}F NMR (for fluorinated compounds) spectra and GCMS data allowed for identification of all reaction products. Conversions of substrates and yields of products were determined from ^{1}H NMR spectra of the reaction mixtures using DMSO as standard. The target products were purified and isolated according to following procedure. The reaction mixture was transferred onto colunm packed with SiO_2 (height of sorbent was 10-15 cm, diameter of column was 1 or 1.5 cm). The fractions obtained by elution with a mixture of dichloromethane/cyclohexane (90 → 0 vol.%) and, whenever necessary, dichloromethane/methanol (0 → 5 vol. %) were analysed by GC-MS and TLC methods and those containing a pure single insertion product were collected and the solvent was removed under reduced pressure. The tagret products were dried and their purity was confirmed by ^{1}H NMR technique.

Carbene N-H insertion of amines in the presence of peripherally substituted ruthenium complex 1β

EDA (127 μL, 1.05 mmol, 2.1 equiv.) was added to a solution of amine (1 M, 0.5 mmol, 1 equiv.) and **1β** (0.5 mM, $1.5 \cdot 10^{-4}$ mmol, 0.05 mol%) in 0.5 mL of dichloromethane under air at 40°C. The reaction mixture was stirred for 1-4 h. The reaction products were analyzed by GC-MS and ^{1}H NMR ($CDCl_3$) techniques. Careful analyses of ^{1}H NMR and ^{19}F NMR (for fluorinated compounds) spectra and GCMS data allowed for identification of all reaction products. Conversions of substrates and yields of products were determined from ^{1}H NMR spectra of the reaction mixtures using DMSO as standard. The target products were purified and isolated according to following procedure. The reaction mixture was transferred onto colunm packed with SiO_2 (height of sorbent was 8-10 cm, diameter of column was 1 or 1.5 cm). The fractions obtained by elution with dichloromethane were analysed by GC-MS and TLC methods and those containing a double insertion product were collected and the solvent was removed under reduced pressure. The minor admixture of side EDA dimerization products was removed at 70°C (10 mmHg) for 30 – 60 min. The tagret products were dried and their purity was confirmed by ^{1}H NMR technique.

Preparation of 2-(methyl(phenyl)amino)acetonitrile, 9

Method (i-iii): To a 3 ml vial containing *N*-methylamine (43.3 μl, 42.9 mg, 0.4 mmol, 1 equiv.) and the complex **1β** (0.49 μg, $4 \cdot 10^{-4}$ mmol, 0.1 mol%) was added an aqueous solution of cyanomethanaminium chloride (3.2 M, 0.5 ml, 1.6 mmol, 4 equiv.) and 100 μl of organic solvent (CH_2Cl_2 for *i*, toluene for *ii*, $C_2H_4Cl_2$ for *iii*) was added. The reaction mixture was flushed with argon and heated to 40ºC. Then, the aqueous solution of $NaNO_2$ (3.84 M, 0.5 ml,1.92 mmol, 4.8 equiv.) was added in 10 portions every 5 min. The obtained mixture was stirred at 40°C for 1 h 20 min and was cooled to room temperature followed by addition of 10 mL of water. The reaction mixture was extracted with dichloromethane (3 x 10 ml), combined organic phases were evaporated and the target product was analyzed by ^{1}H NMR method.

Method (iv): To a 3 ml vial containing *N*-methylamine (54.1 μl, 53.6 mg, 0.5 mmol, 1 equiv.) and the complex **1β** (0.31 μg, $2.5 \cdot 10^{-4}$ mmol, 0.05 mol%) in 100 μl of $C_2H_4Cl_2$ the solution of diazoacetonitrile in $C_2H_4Cl_2$ (0.57 M, 575 μl, 0.55 mmol, 1.1 eqiuv.) was added under Ar at 40°C. The reaction mixture was stirred at 40°C for 1 h. The yield of the target product was determined by ^{1}H NMR method (97 %).

Preparation of ethyl N-(cyanomethyl)-N-(*p*-tolyl)glycinate, 10.

A 3 ml vial was charged with ethyl p-tolylglycinate (67.6 mg, 0.35 mmol, 1 equiv.) and the complex **1β** (213 μg, $1.75 \cdot 10^{-4}$ mmol, 0.05 mol%) dissolved in 100 μl of $C_2H_4Cl_2$. The reaction mixture was heated to

40°C and 688 µl of 0.57 M solution of diazoacetonitrile (1.2 equiv.) in $C_2H_4Cl_2$ was added. The GC-MS and ^1H NMR analyses showed the complete consumption of the starting amine after 1 h. The solvent was removed under reduced pressure and the product was isolated by column chromatography (dichloromethane, SiO_2, height of sorbent – 11 cm, diameter of column – 2 cm). The fractions containing a target product were combined and evaporated under reduced pressure. The tagret product was isolated as a beige solid (70.7 mg, 87%). The product purity was confirmed by GC-MS, ^1H and ^{13}C NMR.

Preparation of diethyl 2,2'-((2-methyl-1,3-phenylene)bis((cyanomethyl)azanediyl))diacetate, 11.

A 3 ml vial was charged with diethyl 2,2'-((2-methyl-1,3-phenylene)bis(azanediyl))diacetate **7ss** (43.9 mg, 0.15 mmol, 1 equiv.), 295 µl of 2 mM solution of **1β** in CH_2Cl_2 ($6 \cdot 10^{-4}$ mmol, 0.40 mol%) and 100 µL of $C_2H_4Cl_2$. The solution was purged with Ar and heated to 40ºC. Then, a 0.57 M solution of diazoacetonitrile in $C_2H_4Cl_2$ was added in four portions every hour (total amount = 4 equiv.). The GC-MS and ^1H NMR analyses showed a complete consumption of the starting diamine after 4 h. The solvents were removed under reduced pressure and the product was isolated by column chromatography (dichloromethane, SiO_2, height of sorbent – 11 cm, diameter of column – 2 cm).The fractions obtained by elution with a mixture of dichloromethane/cyclohexane (50 → 0 vol.%) and dichloromethane/methanol (0 → 3 vol. %) were analysed by GC-MS and TLC. The fractions containing a target product were combined and evaporated under reduced pressure. The tagret product was isolated as a beige solid (31.3 mg, 56%). The product purity was confirmed by GC-MS, ^1H and ^{13}C NMR.

Table S1. Optimization of the reaction of aniline **2a** with EDA catalyzed by the non-peripherally substituted complex **1α.**

Entry	Conditions	Catalyst amount, mol%	Aniline conversion, %	Single N-H insertion, yield **3a**, %	Double N-H insertion, yield **4a**, %
1[a,c]	CH_3CN, 25°C	0.05	29	28	1
2[a,c]	CH_3CN, 60°C	0.05	48	48	0
3[b,c]	CH_2Cl_2, 40°C	0.05	12	12	0
4[a,c]	CH_2Cl_2, 40°C	0.05	35	34	1
5[a,c]	CH_2Cl_2, 40°C	0.10	71	71	0
6[a,c]	CH_2Cl_2, 40°C	0.15	96	96	0
7[a,c]	CH_2Cl_2, 40°C	0.20	100	95	5
8[a,d]	CH_2Cl_2, 40°C	0.15	84	84	0

[a] EDA was added in one portion to start the reaction.

[b] Slow addition of the EDA/aniline mixture to the solution of catalyst.

[c] 2.1 equiv. EDA. [d] 1.1 eq. EDA.

4. NMR spectra and GC/MS data of reaction mixtures and isolated products

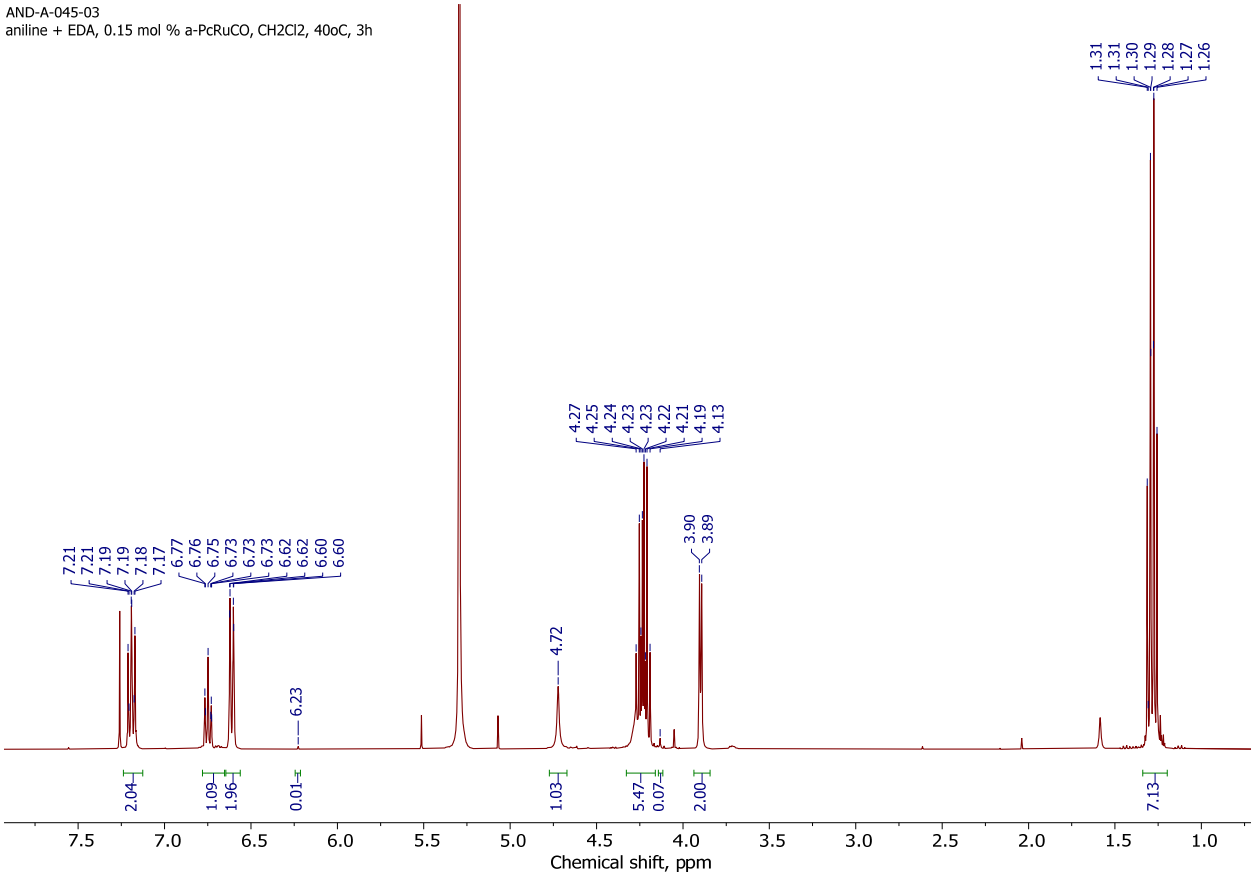


Figure S6. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with aniline **2a** in the presence of 0.15 mol. % **1α**.

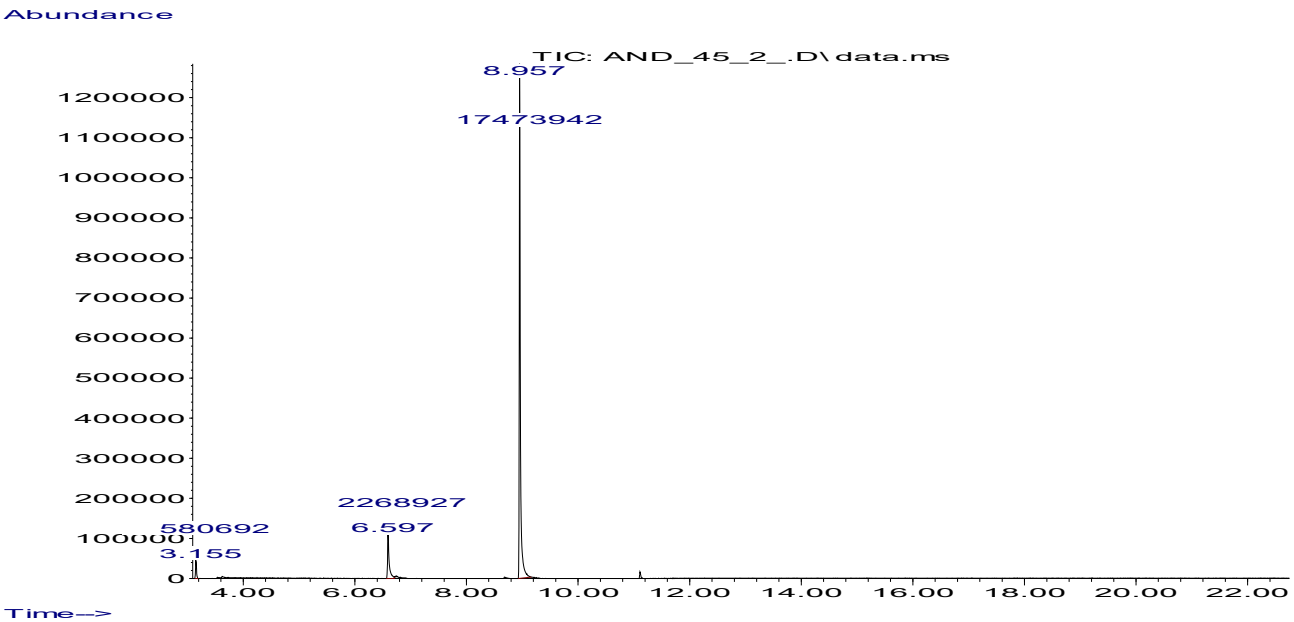
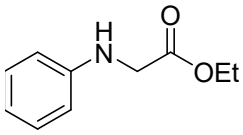


Figure S7. GCMS analysis of the final reaction mixture after reaction of EDA with aniline **2a** in the presence of 0.15 mol. % **1α**.

Ethyl phenylglycinate, 3a



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.23 – 7.15 (m, 2H), 6.80 – 6.72 (m, 1H), 6.62 (dd, J = 8.6, 0.9 Hz, 2H), 4.32 – 4.21 (m, 3H), 3.90 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H).

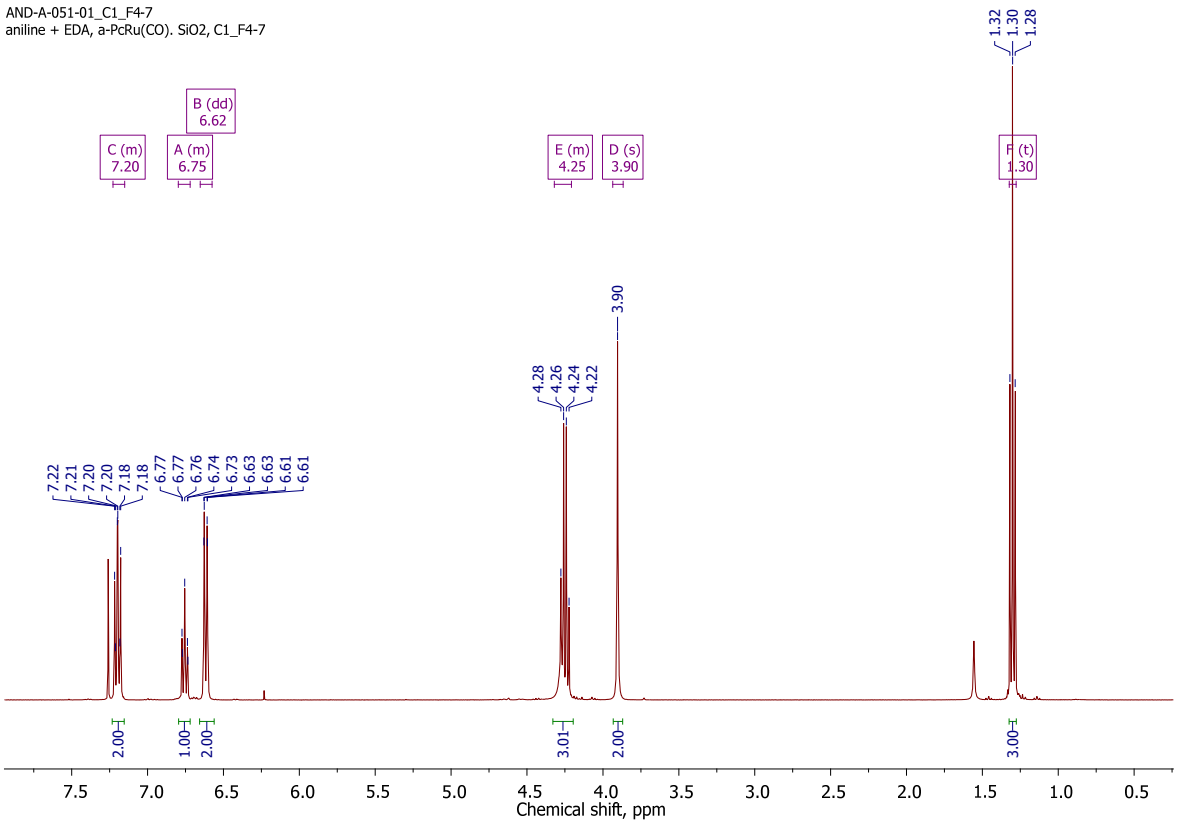


Figure S8. ^{1}H NMR spectrum of isolated ethyl phenylglycinate **3a**.

MS (EI) m/z (%): 179 (17.2), 107 (8.4), 106 (100), 105 (2.8), 104 (8.0), 79 (5.7), 78 (4.1), 77 (20.4), 51 (7.1), 50 (1.9).

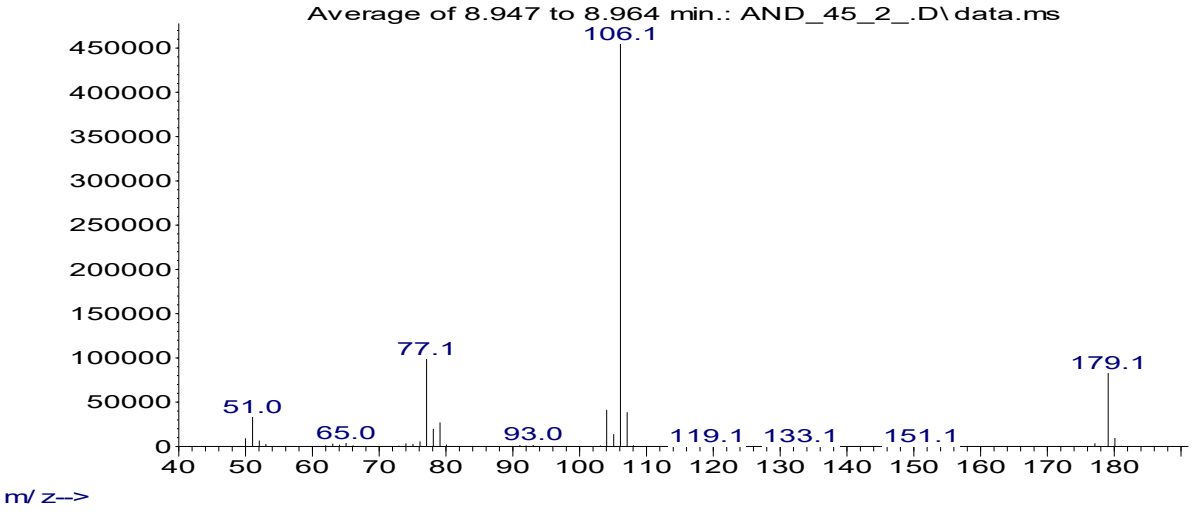


Figure S9. Mass spectrum (EI) of ethyl phenylglycinate **3a**.

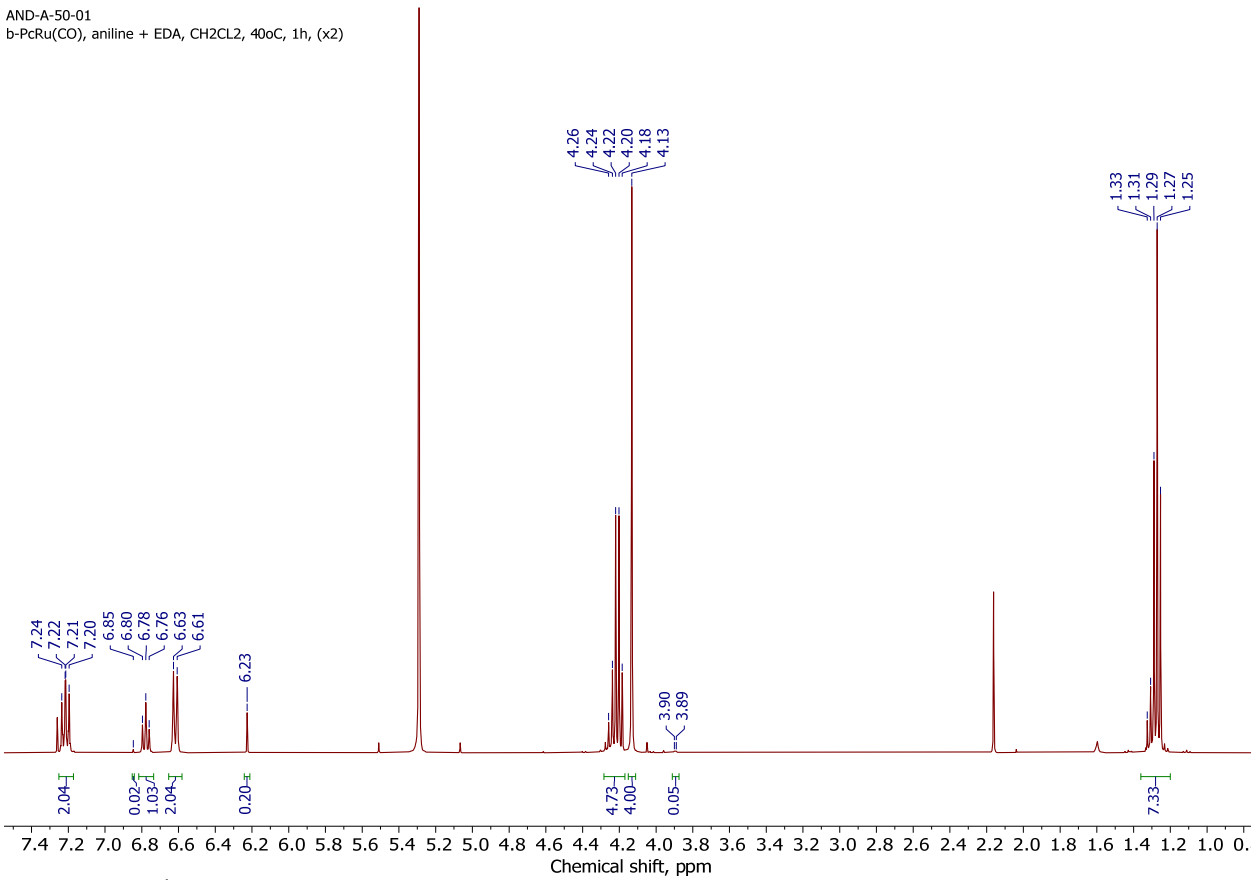


Figure S10. [1]H NMR spectrum of the reaction mixture after reaction of EDA with aniline **2a** in the presence of 0.05 mol. % **1β**.

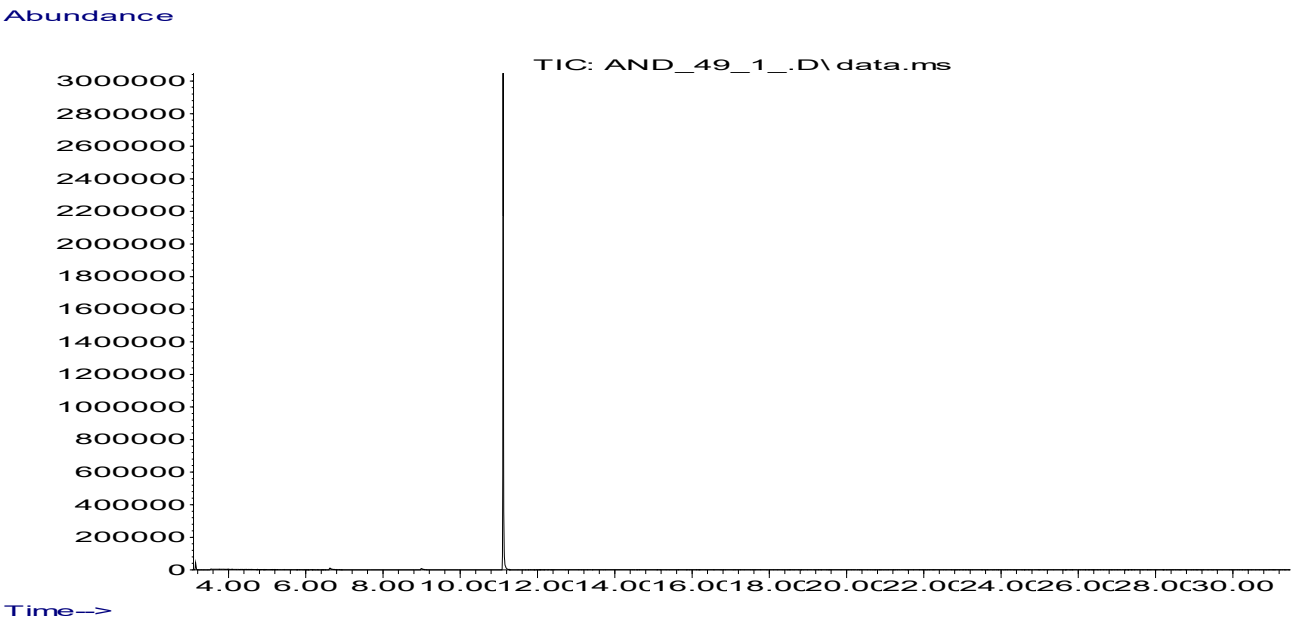
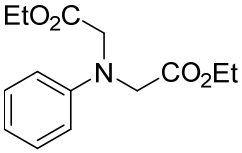


Figure S11. The chromatogram of the reaction mixture after reaction of EDA with aniline **2a** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-(phenylazanediyl)diacetate, 4a



^{1}H NMR (400 MHz, $CDCl_3$) **(**δ, ppm): 7.22 (dd, J = 8.8, 7.4 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 4.22 (q, J = 7.1 Hz, 4H), 4.14 (s, 4H), 1.28 (t, J = 7.1 Hz, 6H).

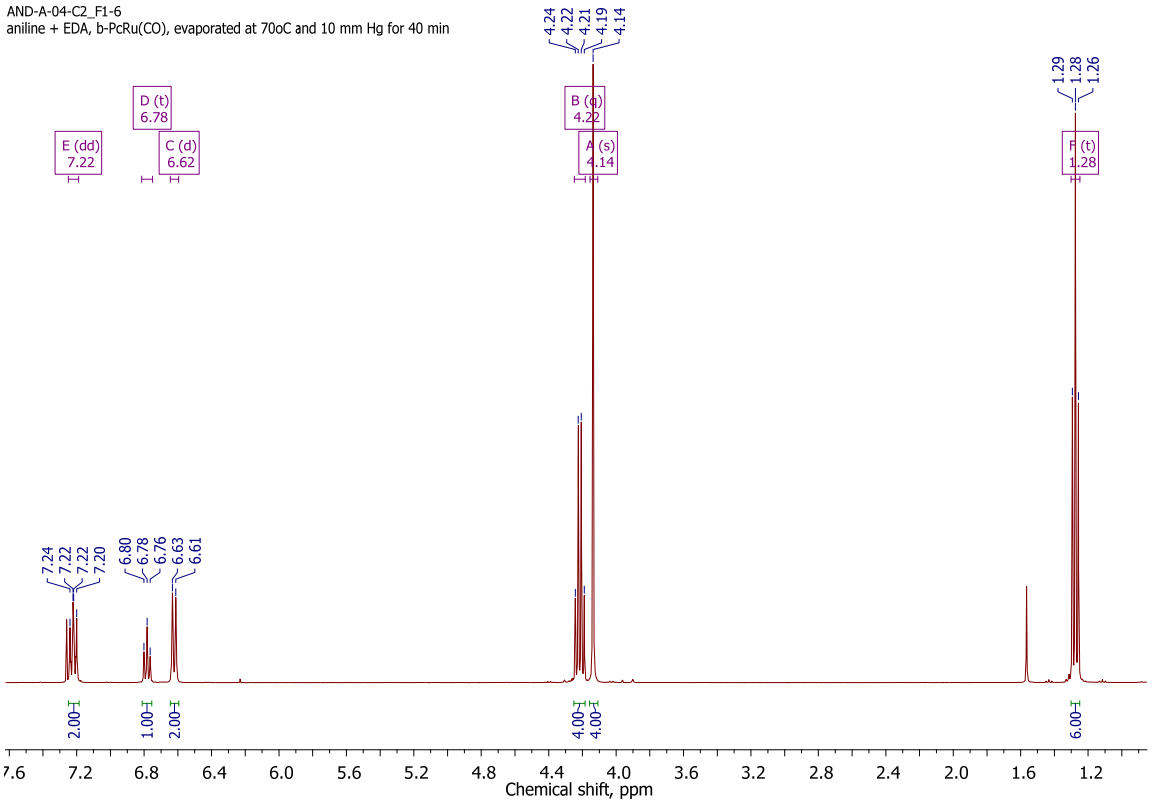


Figure S12. ^{1}H NMR spectrum of diethyl 2,2'-(phenylazanediyl)diacetate **4a**.

MS (EI) m/z (%): 265 (11.3), 193 (14.8), 192 (100), 120 (29.6), 106 (40.4), 105 (10.6), 104 (21.2), 91 (35.4), 77 (25.6), 59 (40.7).

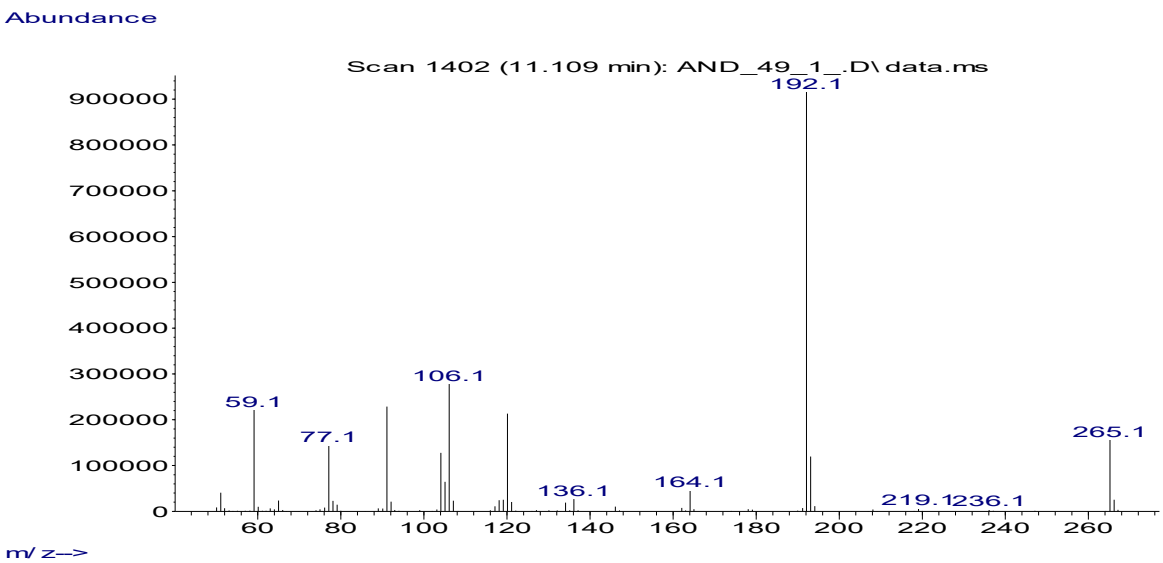


Figure S13. Mass spectrum (EI) of diethyl 2,2'-(phenylazanediyl)diacetate **4a**.

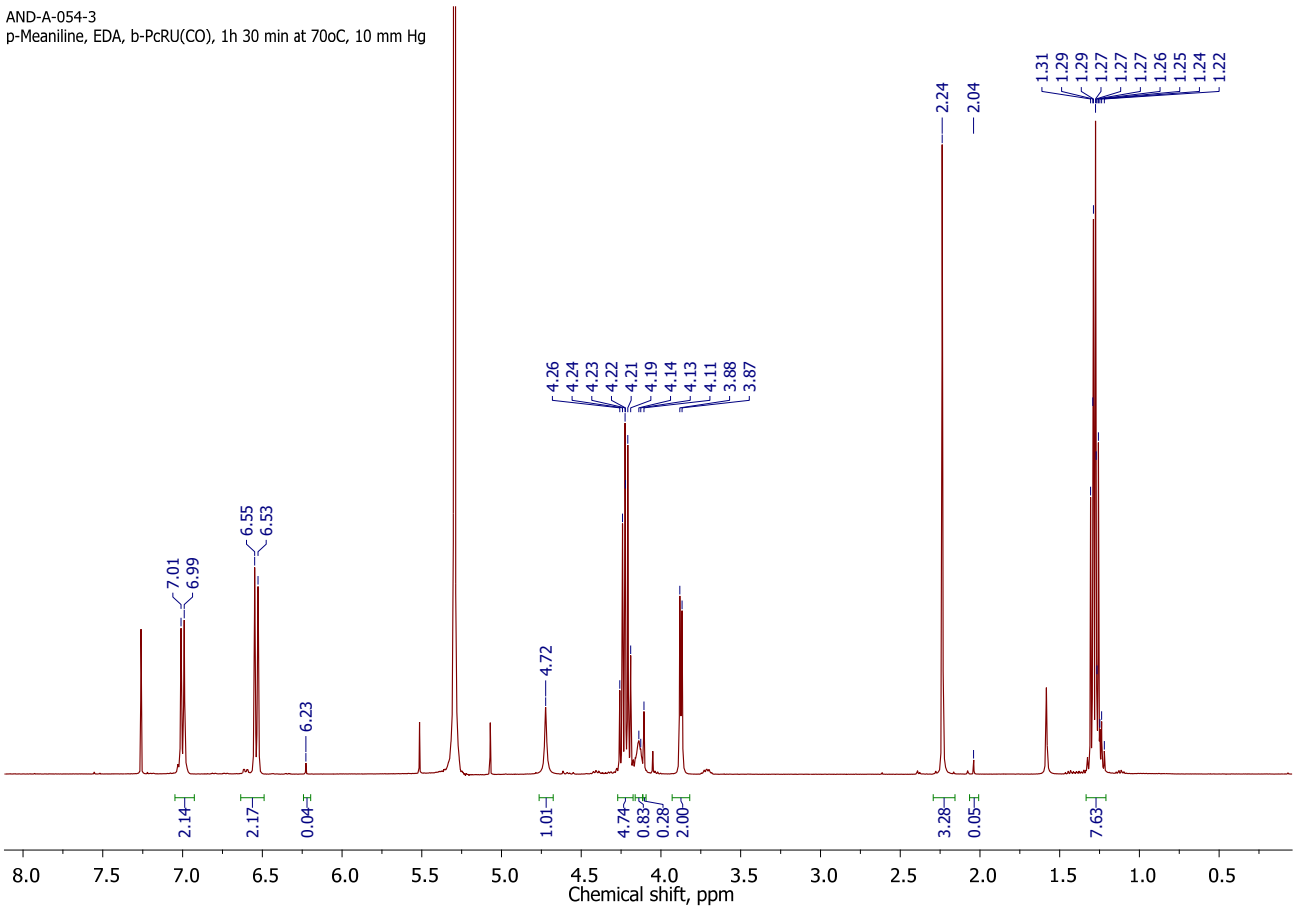


Figure S14. [1]H NMR spectrum of the reaction mixture after reaction of EDA with *p*-toluidine **2b** in the presence of 0.15 mol. % **1α**.

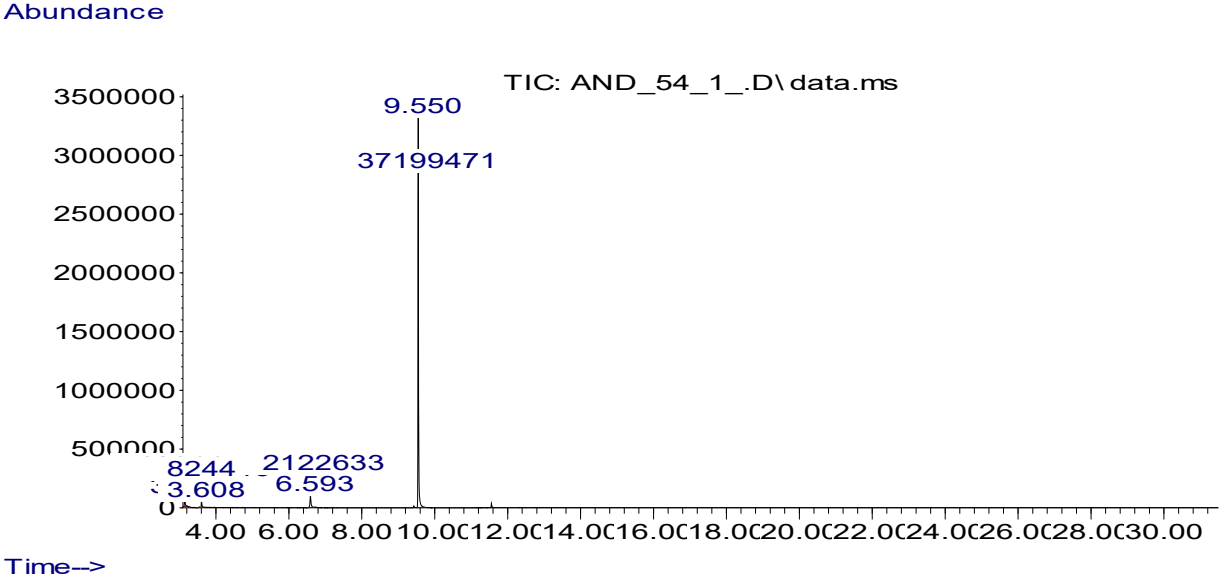
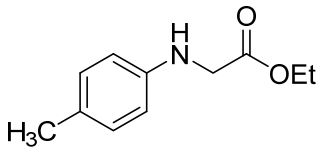


Figure S15. The chromatogram of the reaction mixture after insetion of EDA to *p*-toluidine **2b** in the presence of 0.15 mol. % **1α**.

Ethyl p-tolylglycinate, 3b



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.01 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.14 (s, 1H), 3.88 (s, 2H), 2.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

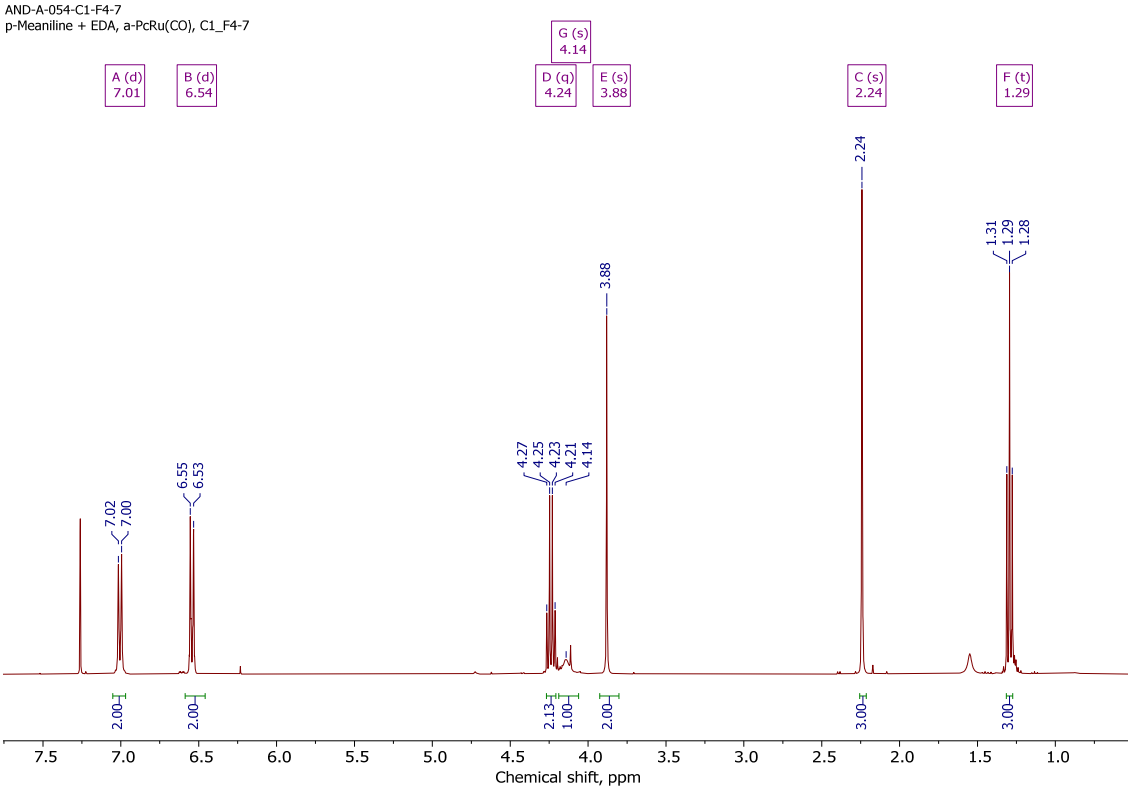


Figure S16. ^{1}H NMR spectrum of ethyl *p*-tolylglycinate **3b**.

MS (EI) m/z (%): 193 (17.3), 121 (9.3), 120 (100), 119 (3.7), 118 (9.4), 92 (3.8), 91 (17.7), 89 (3.3), 77 (3.1), 65 (7.9).

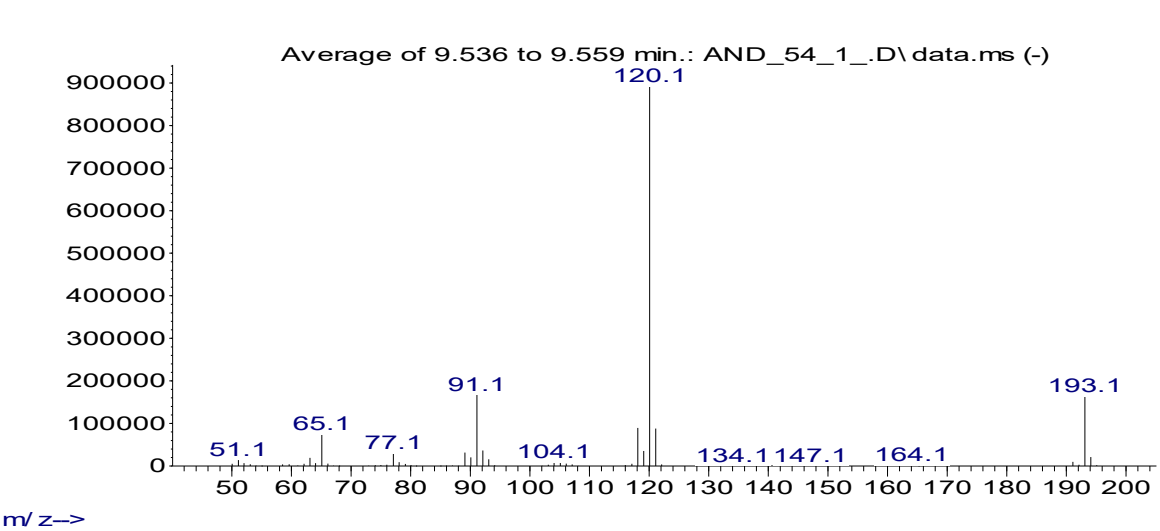


Figure S17. Mass spectrum (EI) of ethyl *p*-tolylglycinate **3b**.

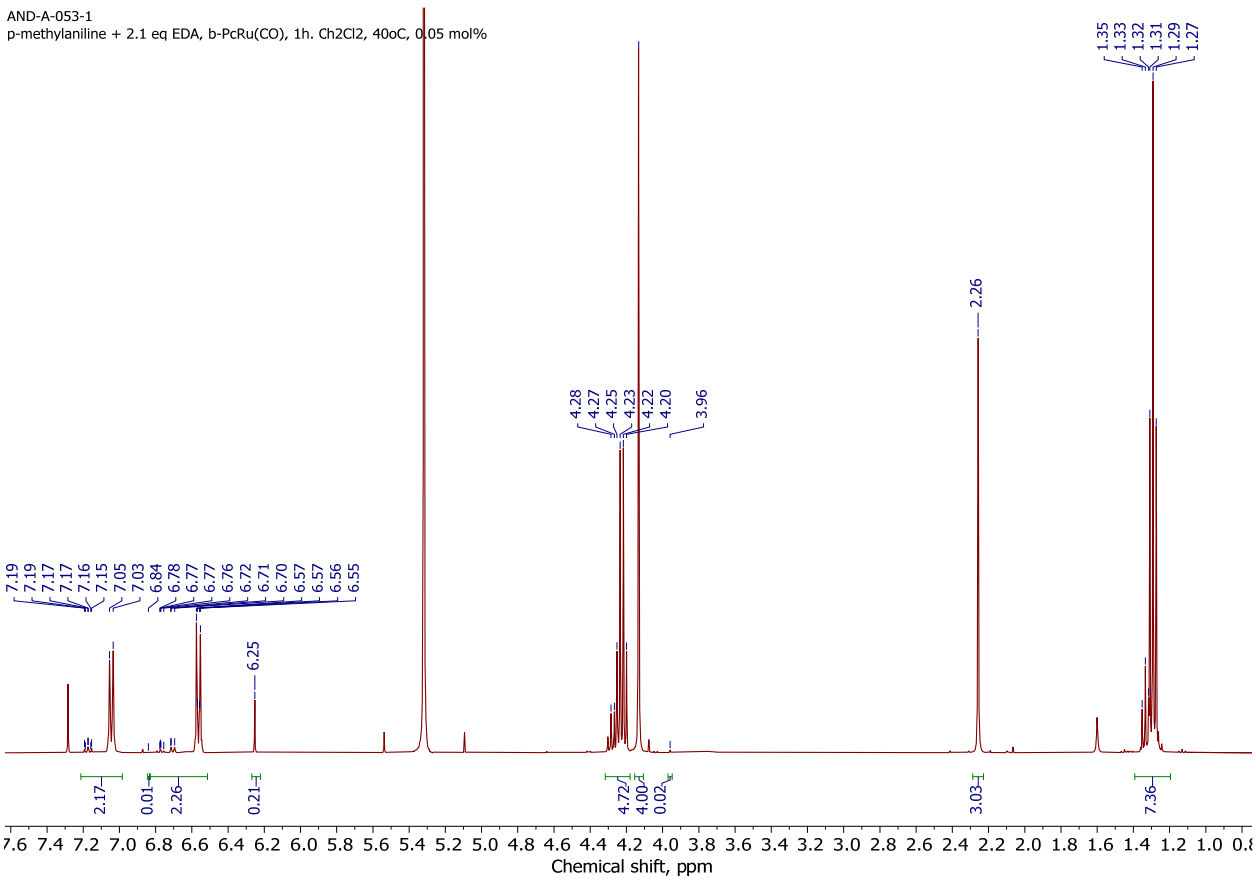


Figure S18. [1]H NMR spectrum of the reaction mixture after reaction of EDA with *p*-toluidine **2b** in the presence of 0.05 mol. % **1β**.

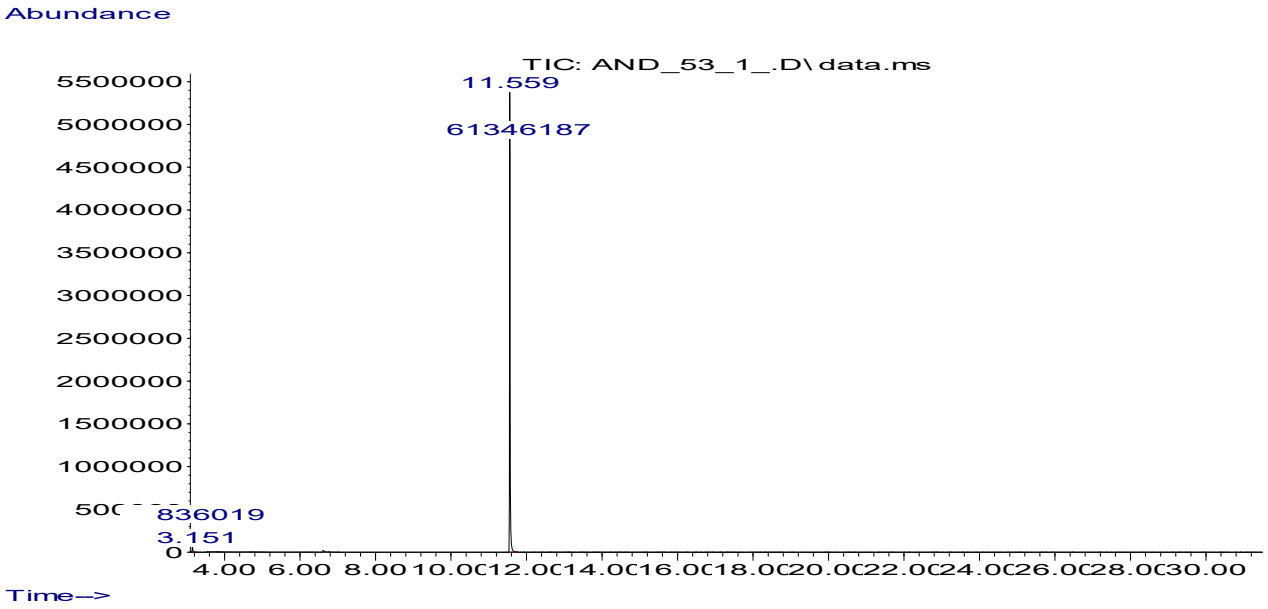
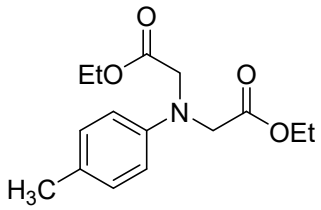


Figure S19. Chromatogram of reaction mixture after reaction of EDA with *p*-toluidine **2b** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-(*p*-tolylazanediyl)diacetate, 4b



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.02 (d, *J* = 8.2 Hz, 2H), 6.58 – 6.50 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 4H), 4.11 (s, 4H), 2.24 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H).

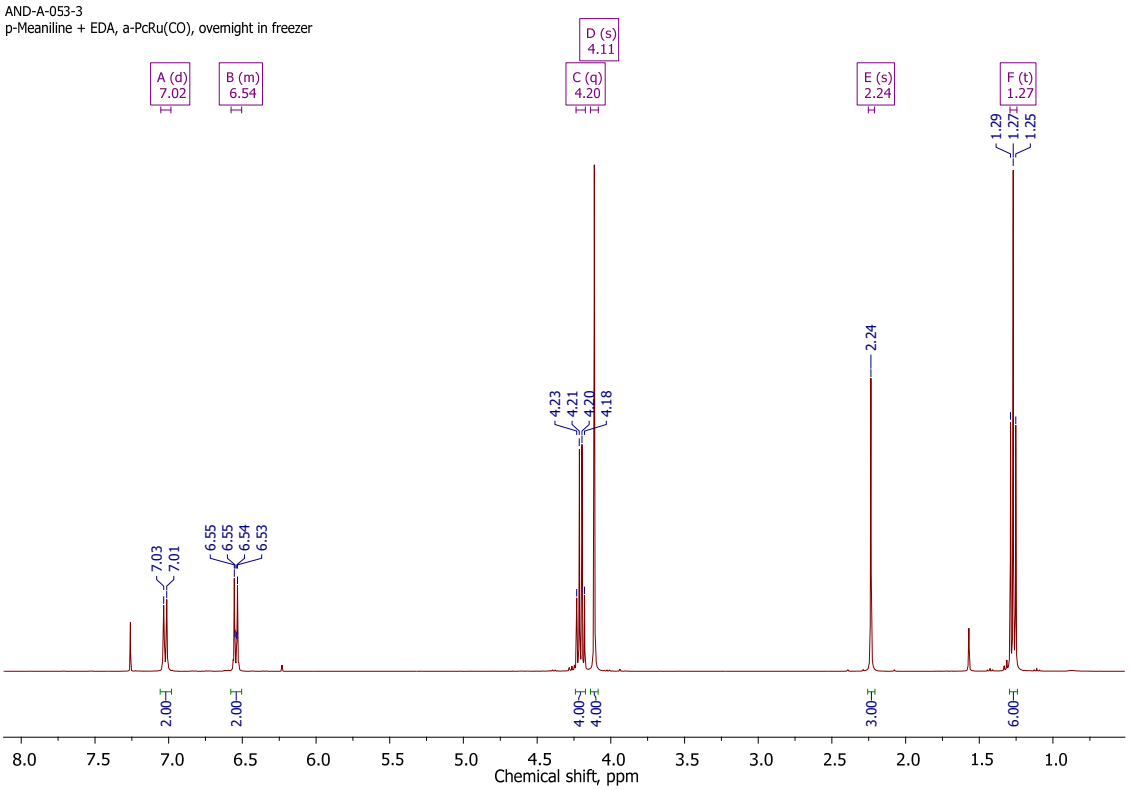


Figure S20. ^{1}H NMR spectrum of diethyl 2,2'-(*p*-tolylazanediyl)diacetate **4b**.

MS (EI) m/z (%): 279 (19.2), 207 (13.9), 206 (100), 134 (23.2), 120 (25.7), 119 (10.1), 118 (17.4), 105 (16.6), 91 (19.0), 59 (19.1).

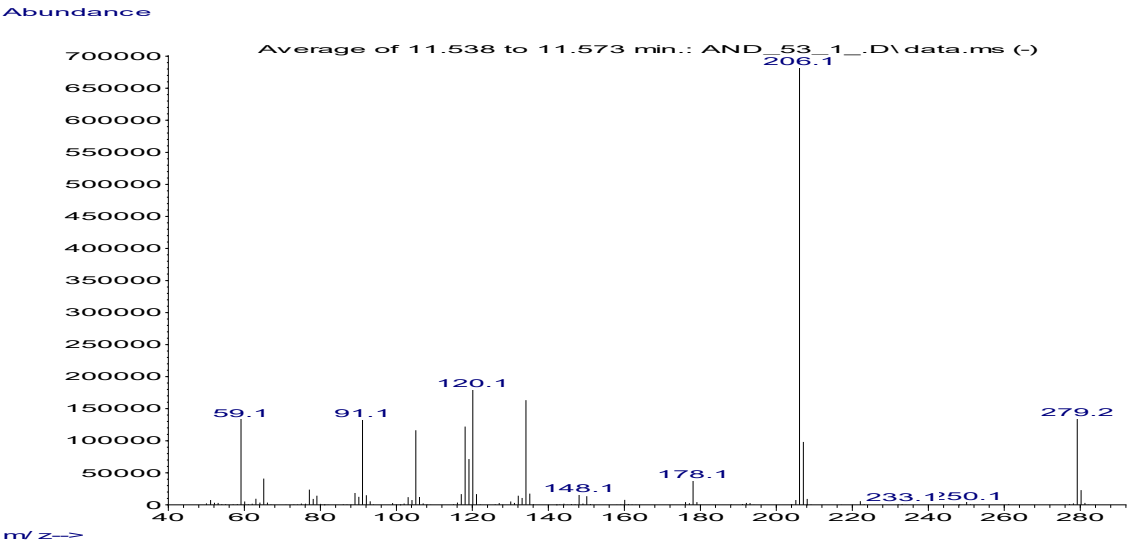


Figure S21. Mass spectrum (EI) of diethyl 2,2'-(*p*-tolylazanediyl)diacetate **4b**.

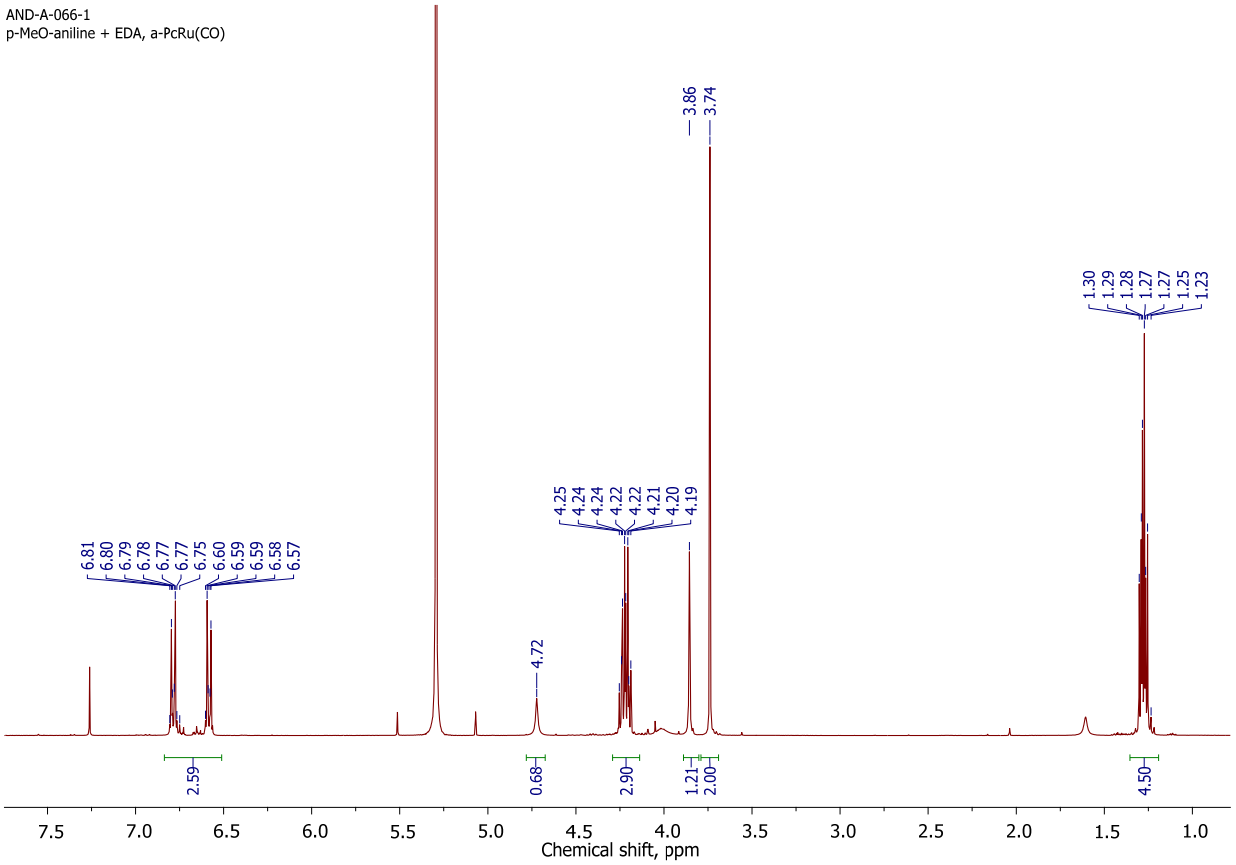


Figure S22. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 4-methoxyaniline **2c** in the presence of 0.15 mol. % **1α**.

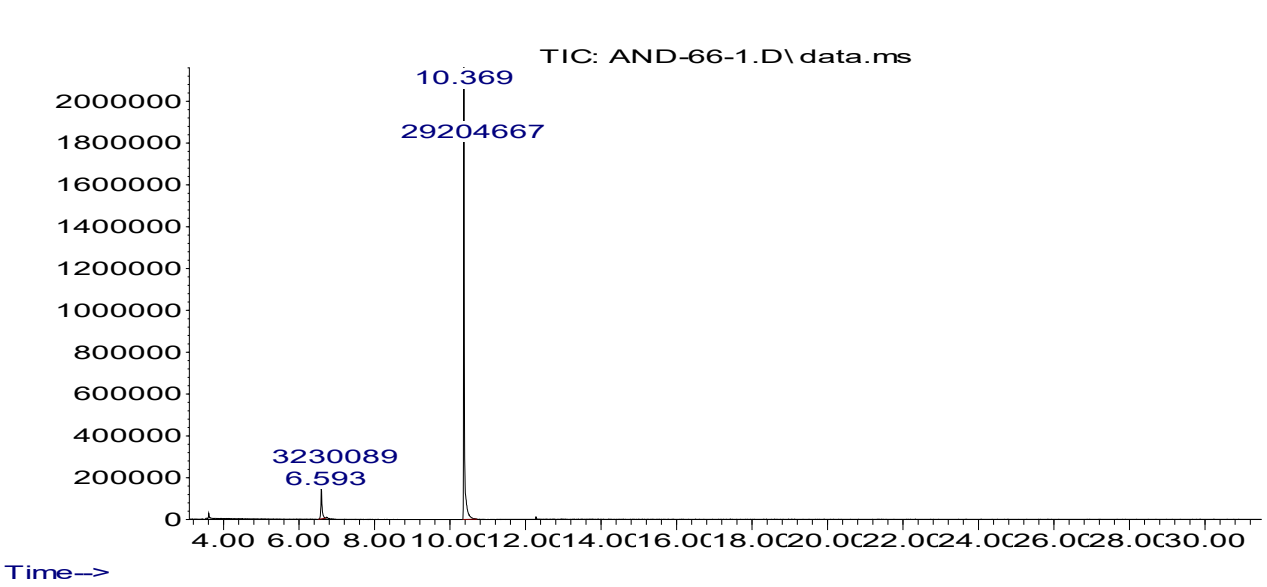
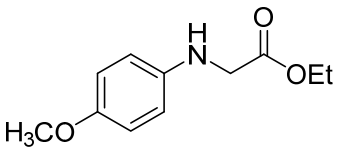


Figure S23. Chromatogram of the reaction mixture after insertion of EDA 4-methoxyaniline **2c** in the presence of 0.15 mol. % **1α**.

Ethyl (4-methoxyphenyl)glycinate, 3c



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.82 – 6.77 (m, 2H), 6.62 – 6.55 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.86 (s, 2H), 3.75 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).

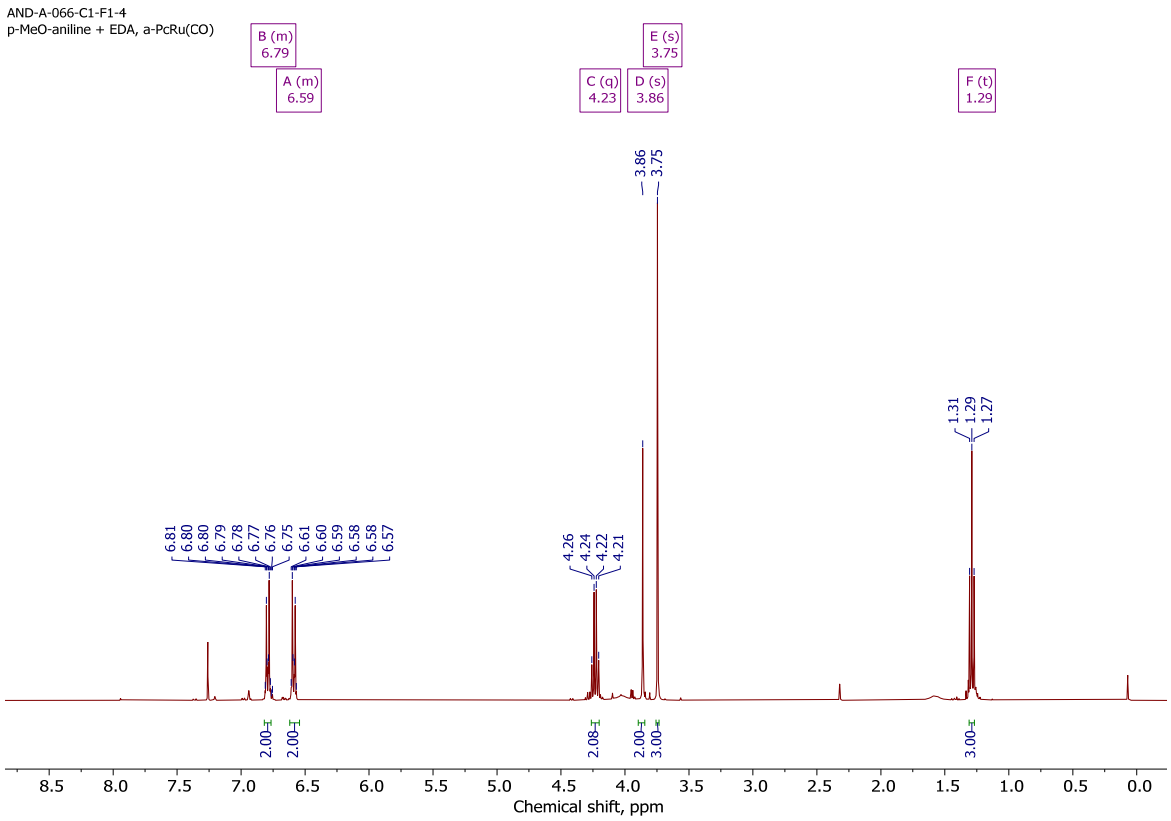


Figure S24. ^{1}H NMR spectrum of ethyl (4-methoxyphenyl)glycinate **3c.**

MS (EI) m/z (%): 209 (20.3), 137 (9.1), 136 (100), 134 (11.6), 121 (8.3), 120 (8.2), 108 (5.2), 93 (3.8), 92 (6.2), 77 (5.6).

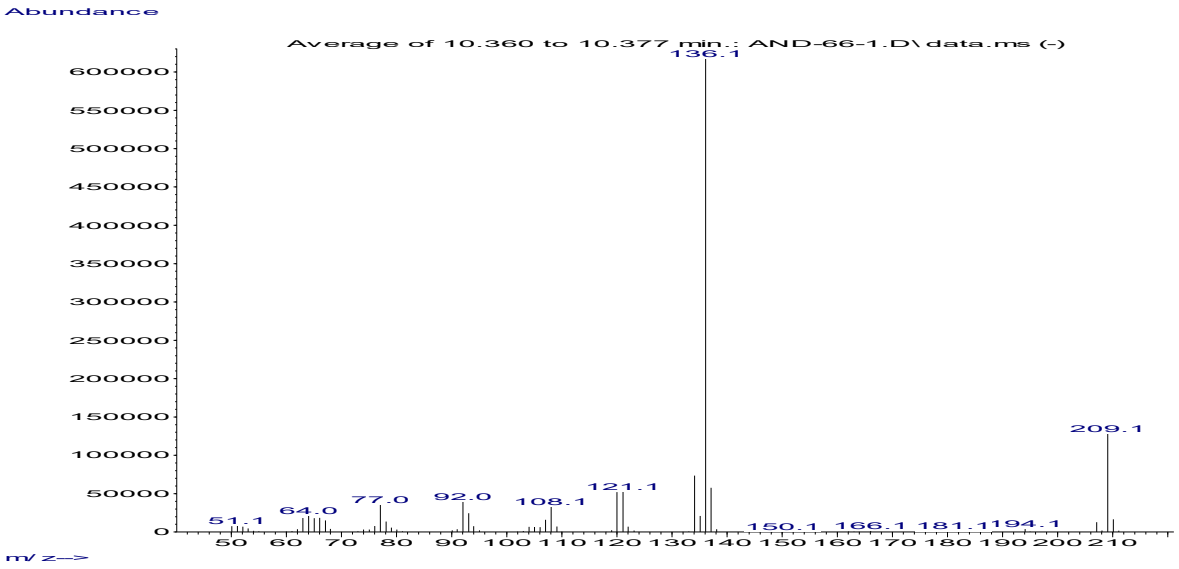


Figure S25. Mass spectrum (EI) of ethyl (4-methoxyphenyl)glycinate **3c**.

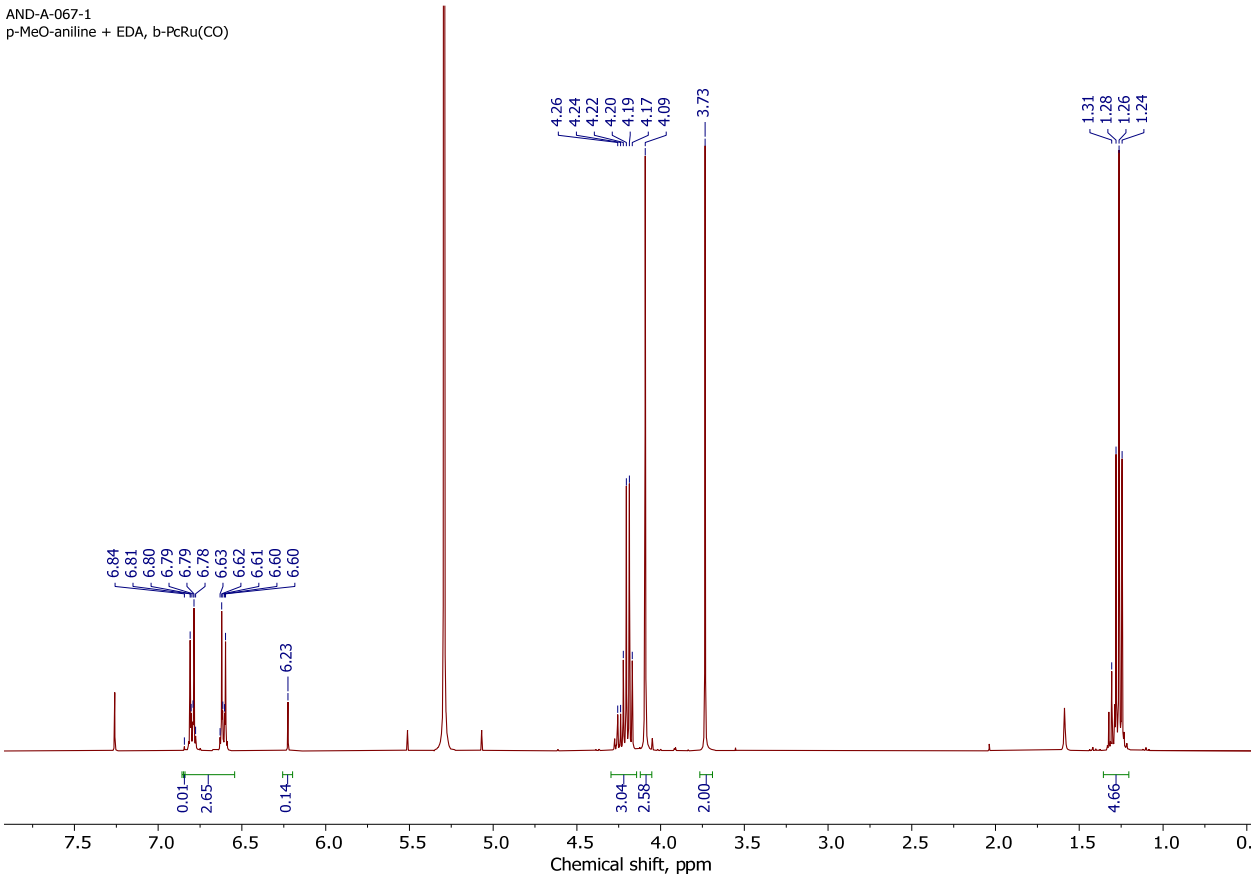


Figure S26. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 4-methoxyaniline **2c** in the presence of 0.05 mol. % **1β**.

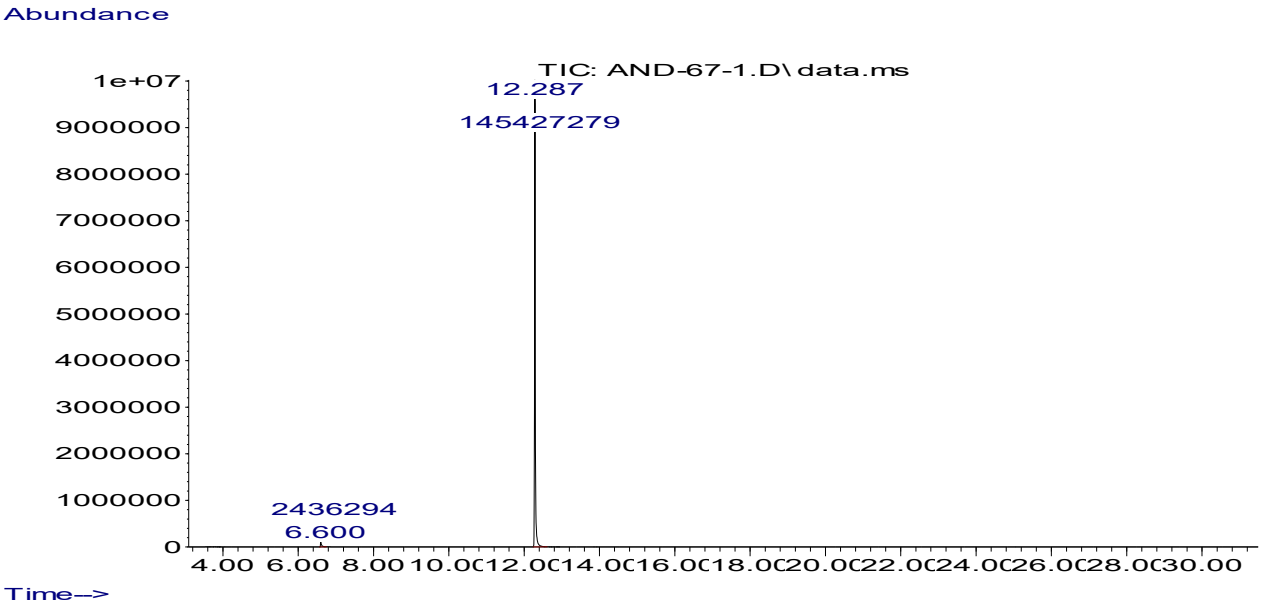
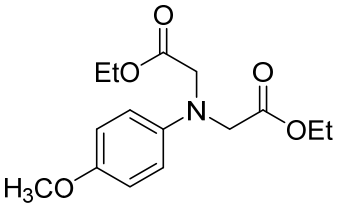


Figure S27. Chromatogram of the reaction mixture after reaction of EDA with 4-methoxyaniline **2c** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((4-methoxyphenyl)azanediyl)diacetate, 4c



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.77 – 6.70 (m, 2H), 6.58 – 6.52 (m, 2H), 4.13 (q, J = 7.1 Hz, 4H), 4.03 (s, 4H), 3.67 (s, 3H), 1.20 (t, J = 7.1 Hz, 6H).

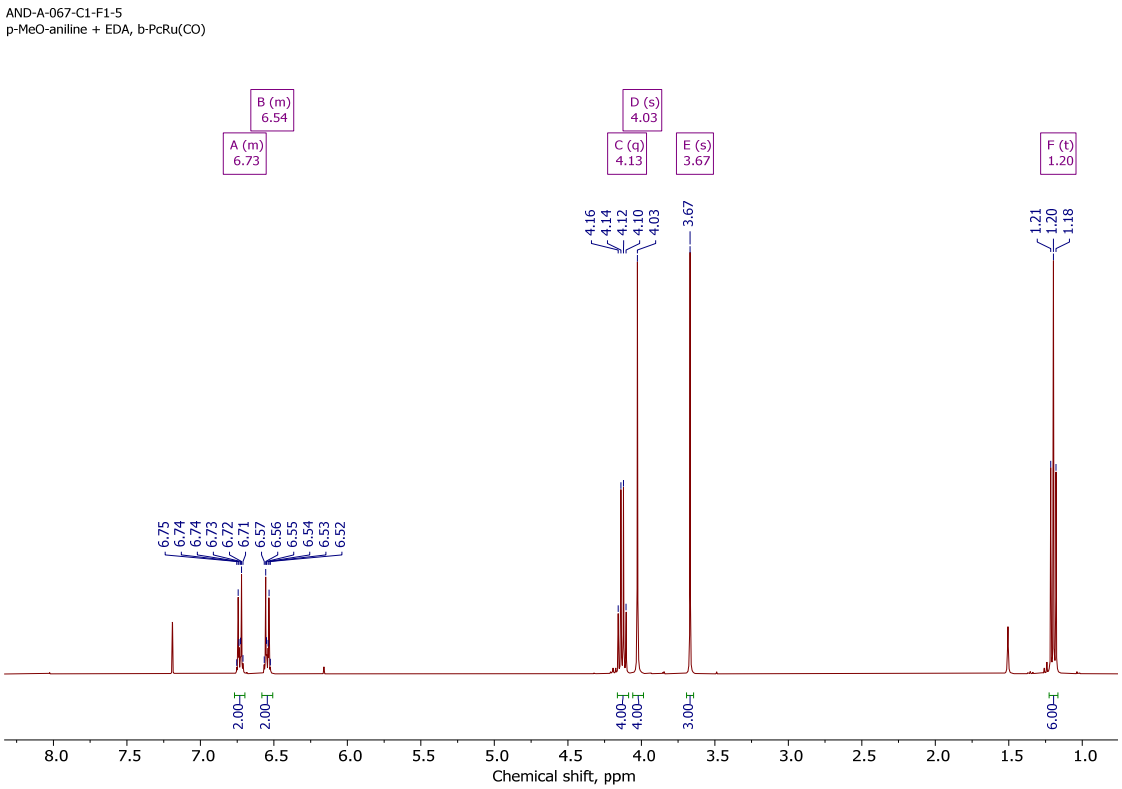


Figure S28. ^{1}H NMR spectrum of diethyl 2,2'-((4-methoxyphenyl)azanediyl)diacetate **4c**.

MS (EI) m/z (%): 295 (25.4), 223 (14.1), 222 (100), 150 (20.7), 120 (24.9), 136 (18.8), 135 (19.0), 134 (10.0), 121 (11.1), 59 (17.5).

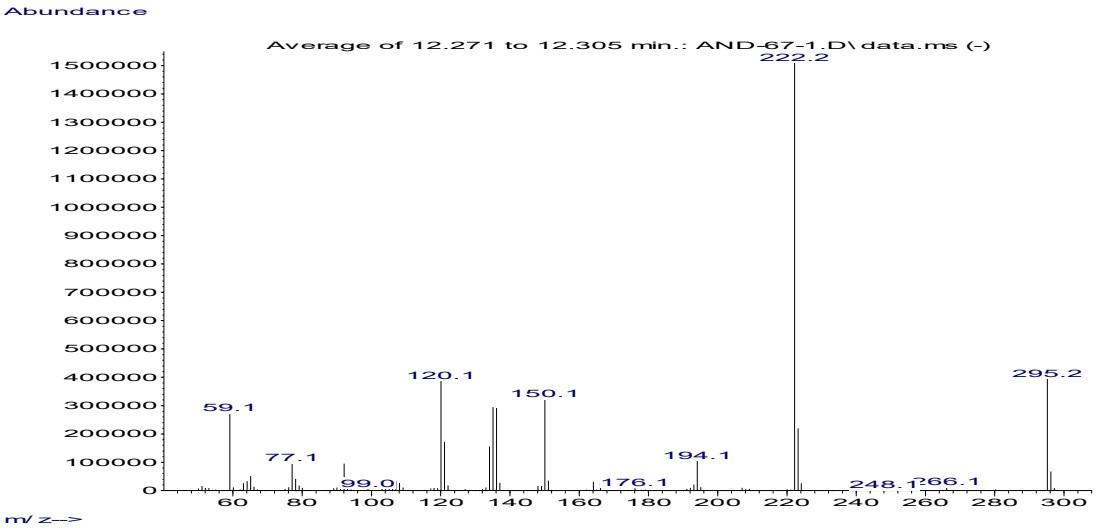


Figure S29. Chromatogram of diethyl 2,2'-((4-methoxyphenyl)azanediyl)diacetate **4c**.

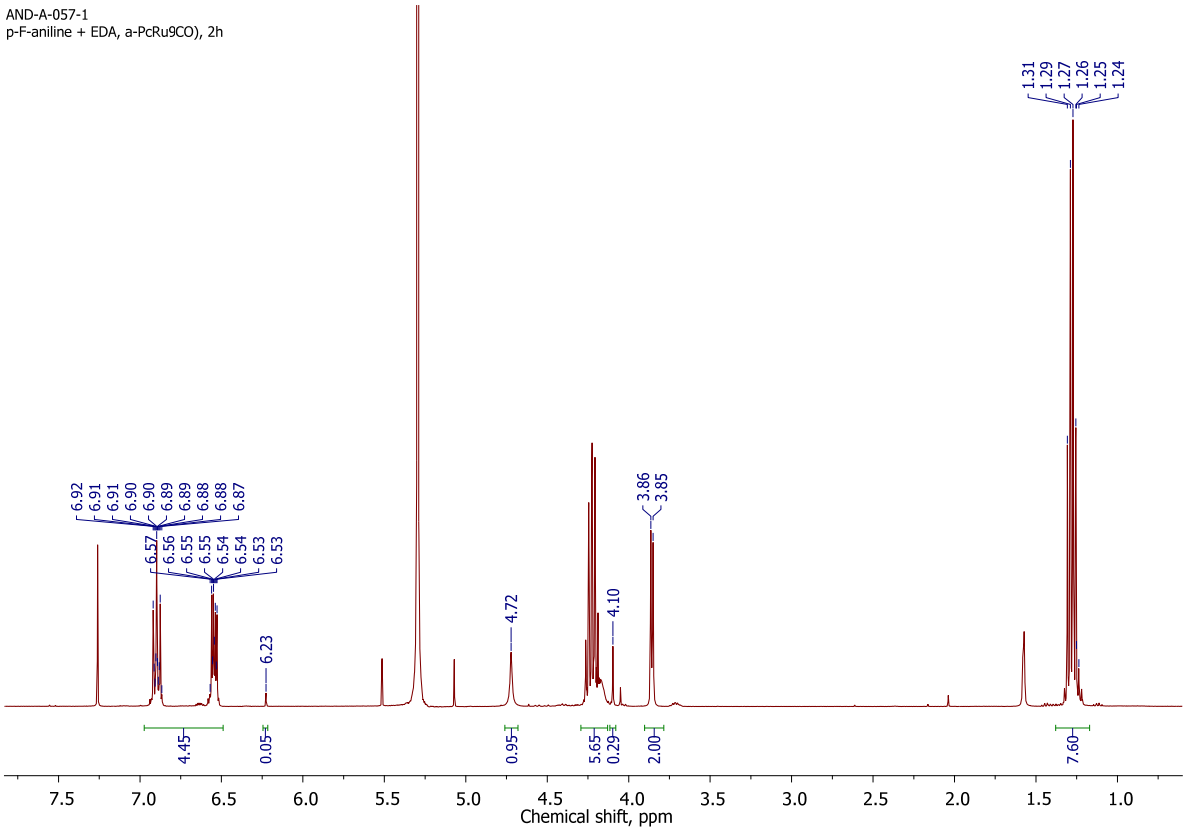


Figure S30. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 4-fluoroaniline **2d** in the presence of 0.15 mol. % **1α**.

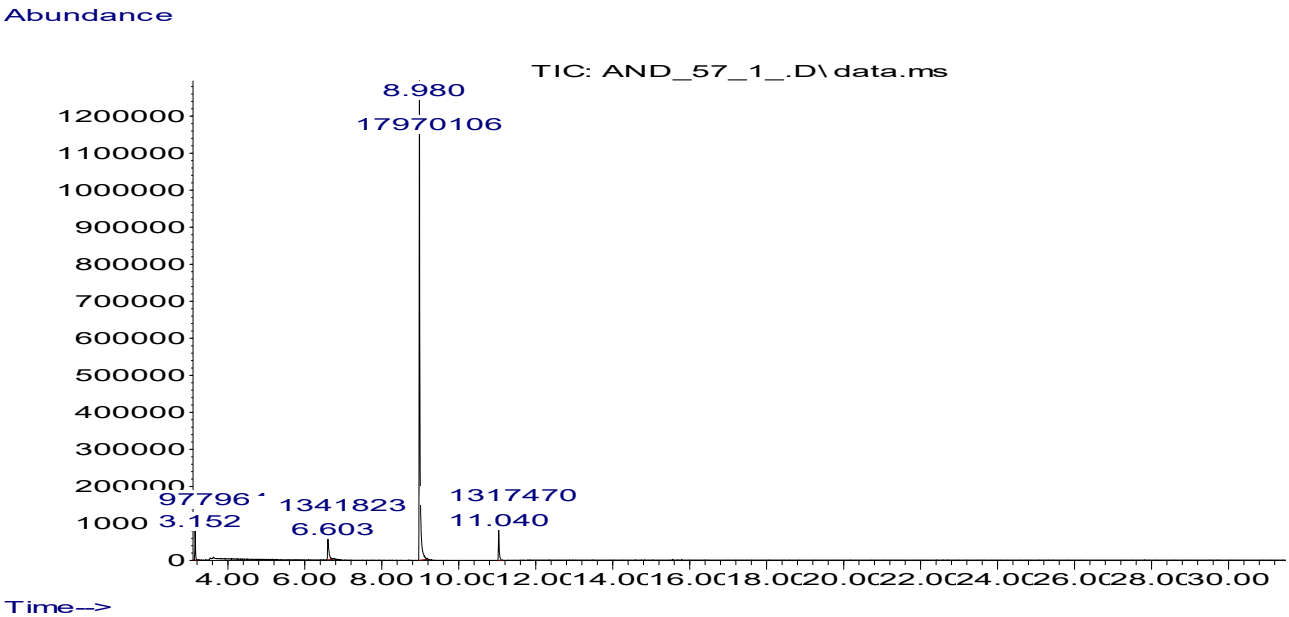
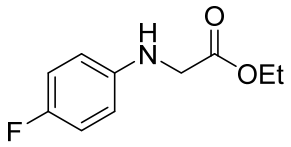


Figure S31. Chromatogram of the reaction mixture after reaction of EDA with 4-fluoroaniline **2d** in the presence of 0.15 mol. % **1α**.

Ethyl (4-fluorophenyl)glycinate, 3d



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.98 – 6.83 (m, 2H), 6.59 – 6.50 (m, 2H), 4.24 (q, J = 7.1 Hz, 2H), 4.17 (s, 1H), 3.86 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H).

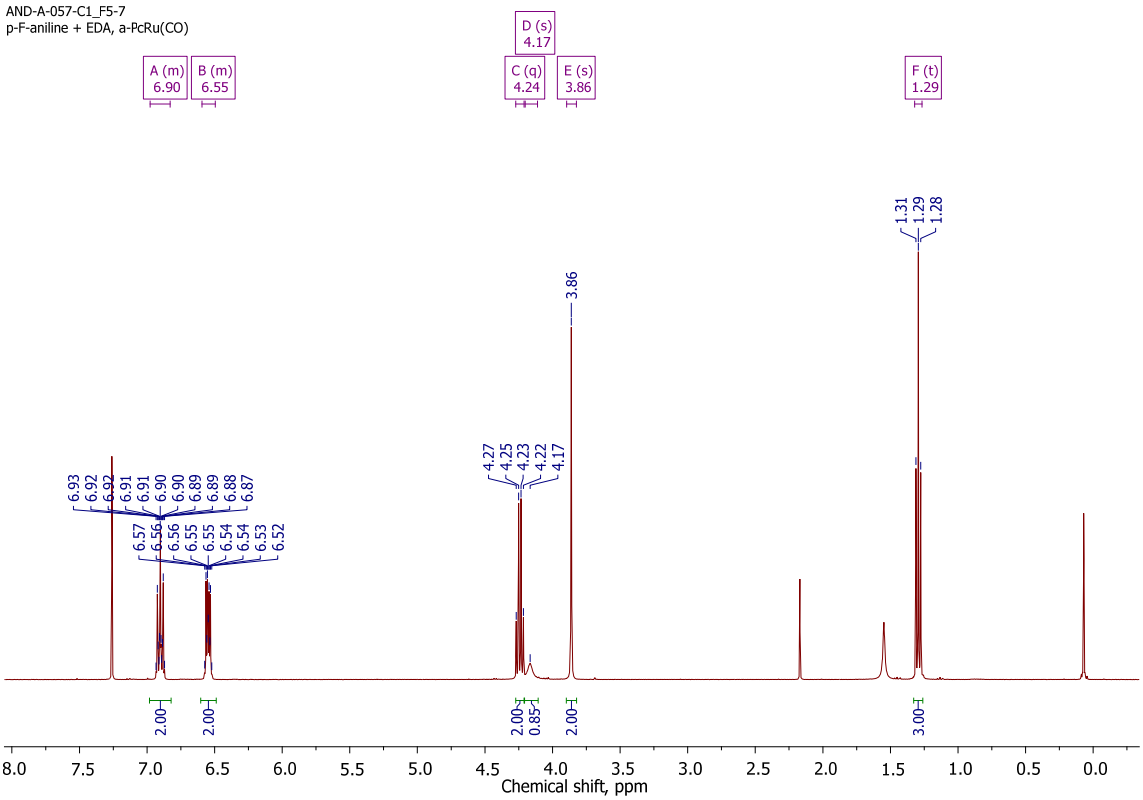


Figure S32. ^{1}H NMR spectrum of ethyl (4-fluorophenyl)glycinate **3d**.

MS (EI) m/z (%): 197 (14.0), 125 (8.1), 124 (100), 123 (3.4), 122 (10.9), 97 (4.8), 96 (7.4), 95 (13.9), 77 (2.1), 75 (7.3).

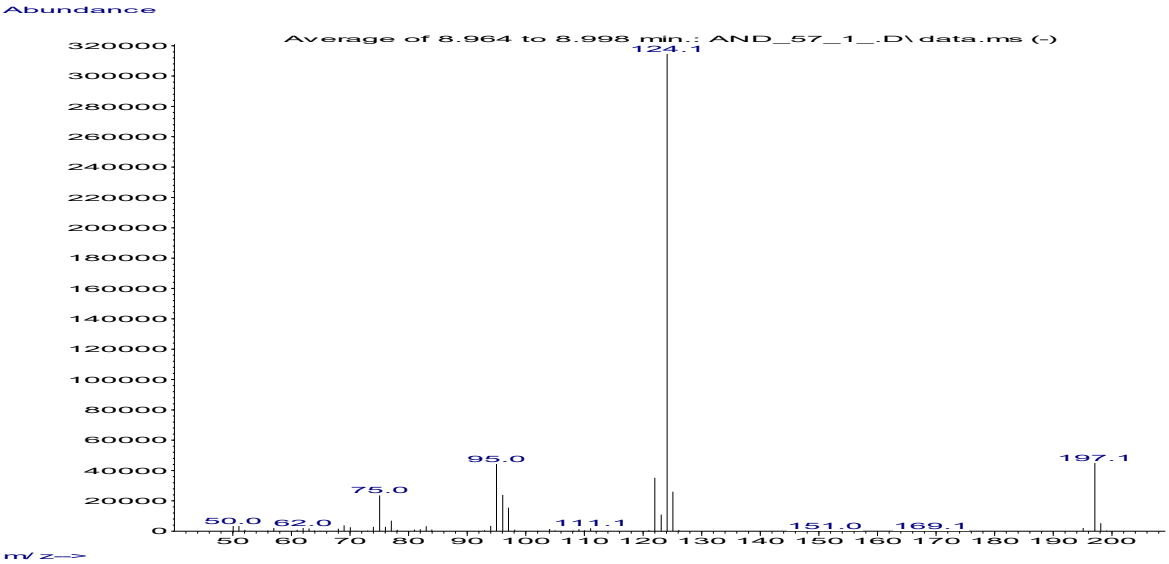


Figure S33. Mass spectrum (EI) of ethyl (4-fluorophenyl)glycinate **3d**.

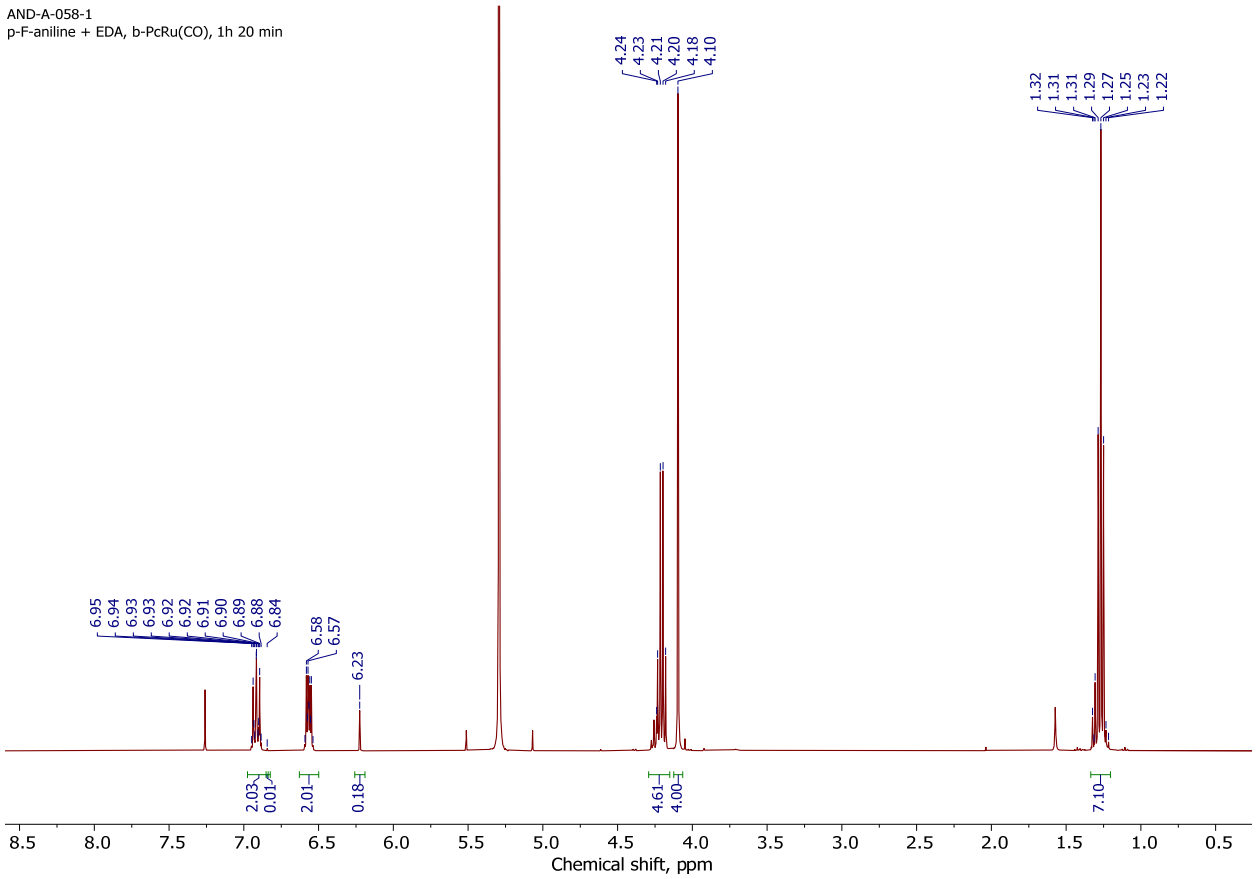


Figure S34. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 4-fluoroaniline **2d** in the presence of 0.05 mol. % **1β**.

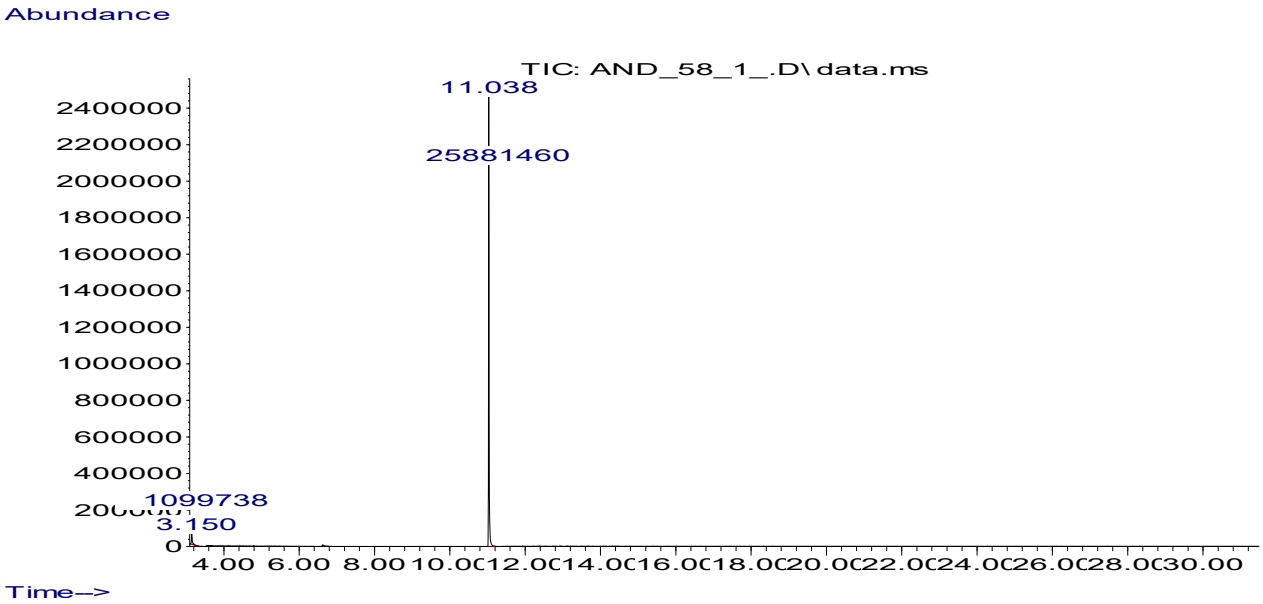
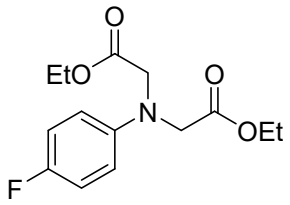


Figure S35. Chromatogram of the reaction mixture after reaction of 4- fluoroaniline **2d** with EDA in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((4-fluorophenyl)azanediyl)diacetate, 4d



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.90 – 6.78 (m, 2H), 6.53 – 6.44 (m, 2H), 4.14 (q, J = 7.1 Hz, 4H), 4.03 (s, 4H), 1.20 (t, J = 7.1 Hz, 6H).

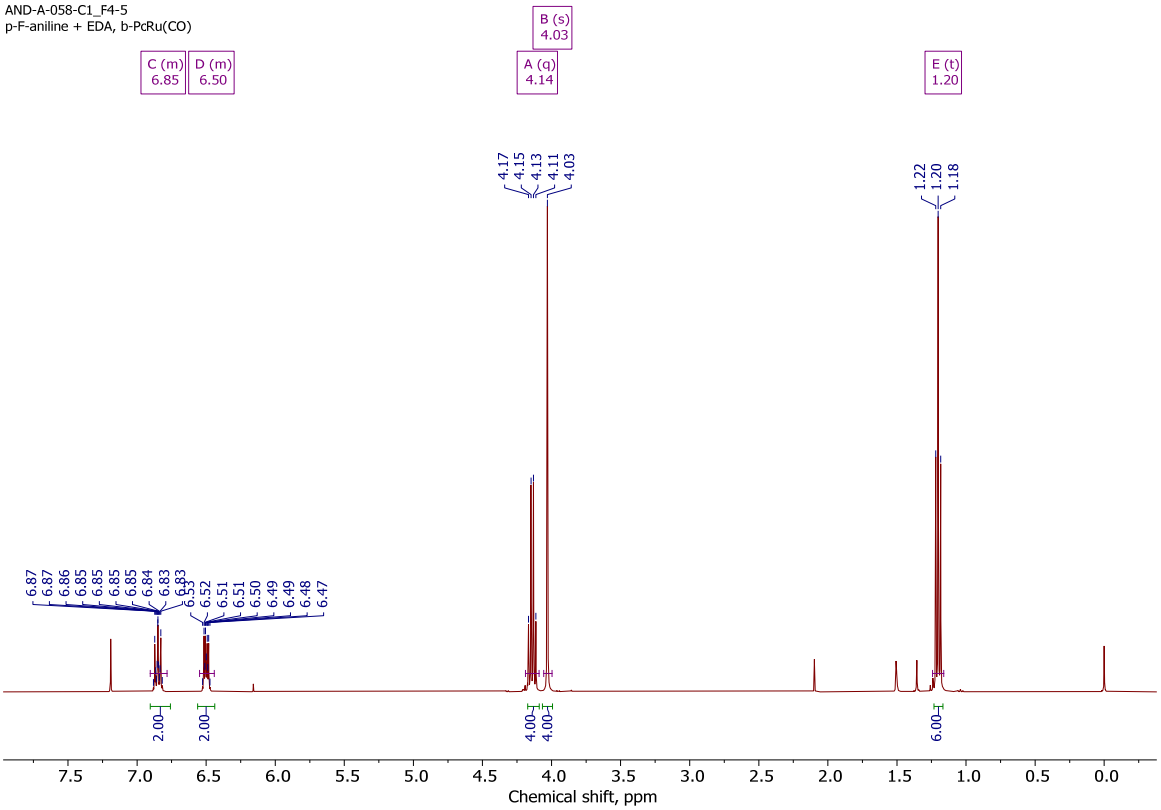


Figure S36. ^{1}H NMR spectrum of diethyl 2,2'-((4-fluorophenyl)azanediyl)diacetate **4d**.

MS (EI) m/z (%): 283 (15.7), 211 (12.6), 210 (100), 138 (17.6), 124 (34.0), 123 (10.2), 122 (20.7), 109 (26.5), 95 (15.4), 59 (36.6).

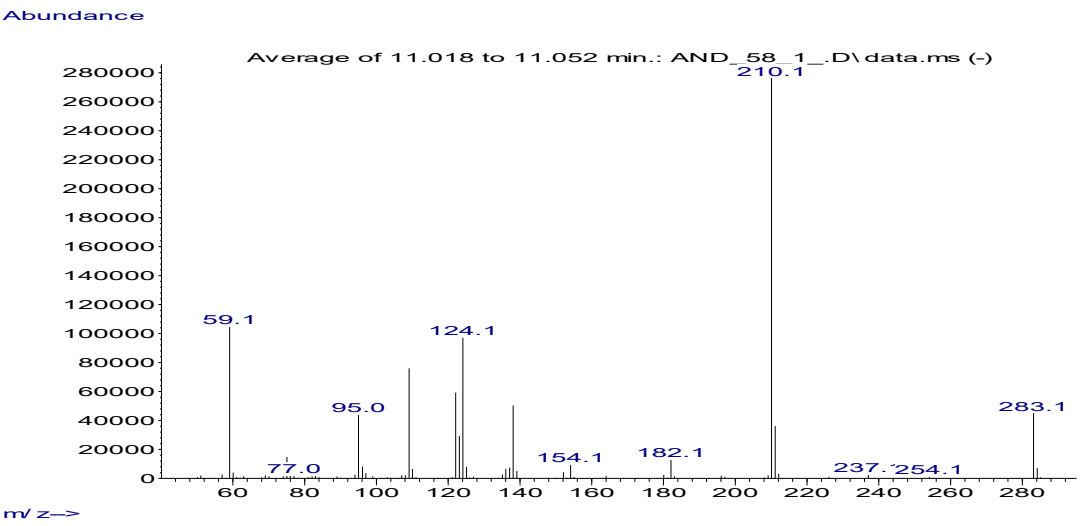


Figure S37. Mass spectrum (EI) of diethyl 2,2'-((4-fluorophenyl)azanediyl)diacetate **4d**.

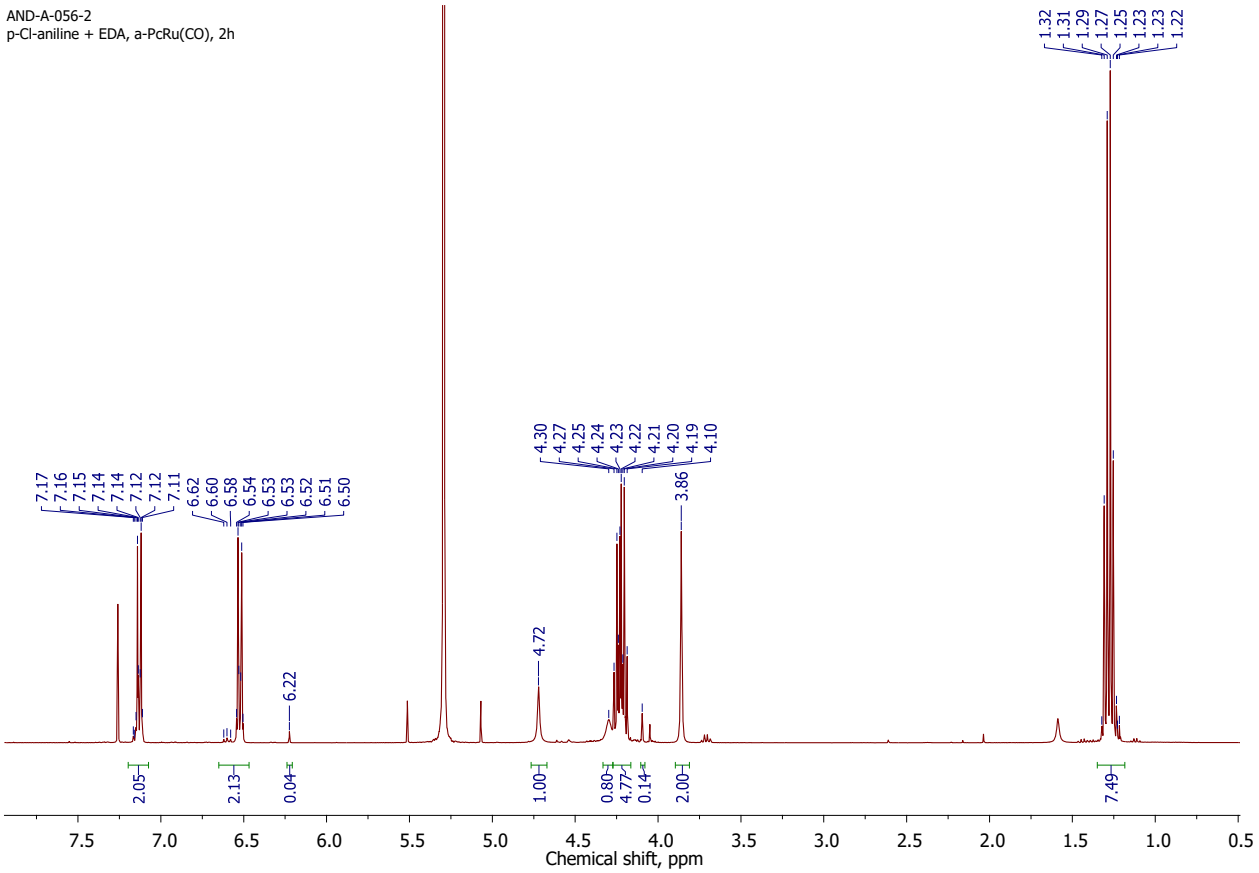


Figure S38. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 4-chloroaniline **2e** in the presence of 0.15 mol. % **1α**.

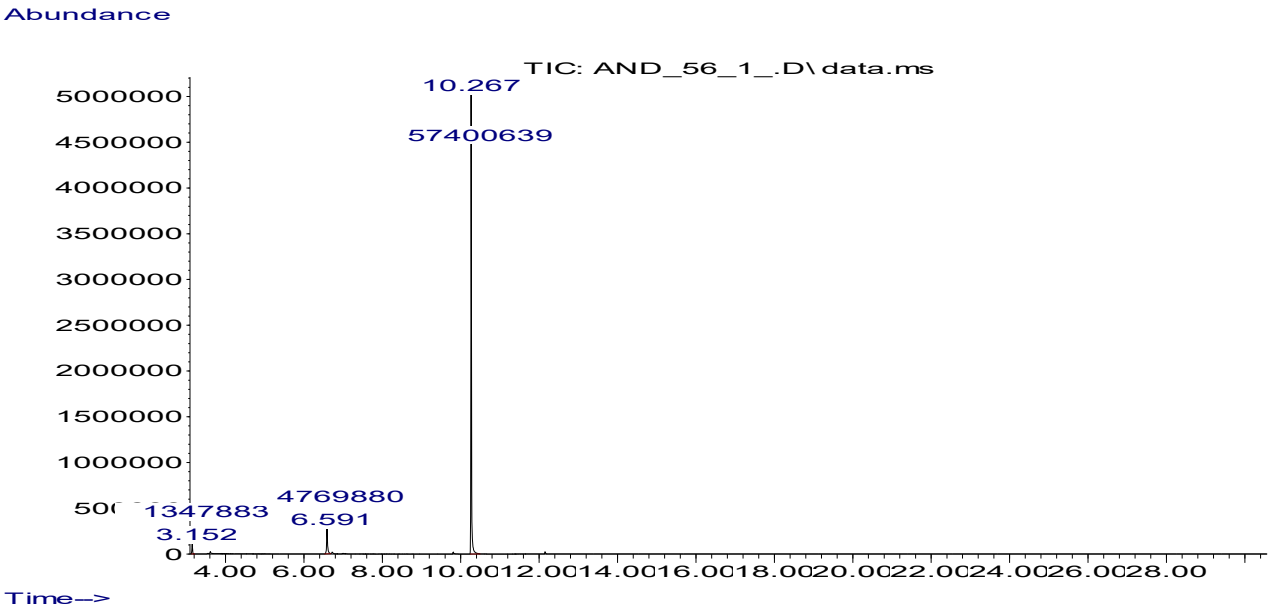
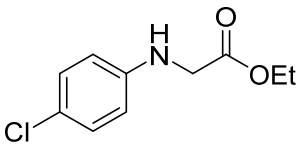


Figure S39. Chromatogram of the reaction mixture after reaction of EDA with 4-chloroaniline **2e** in the presence of 0.15 mol. % **1α**.

Ethyl (4-chlorophenyl)glycinate 3e



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.17 – 7.10 (m, 2H), 6.56 – 6.50 (m, 2H), 4.29 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.87 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H).

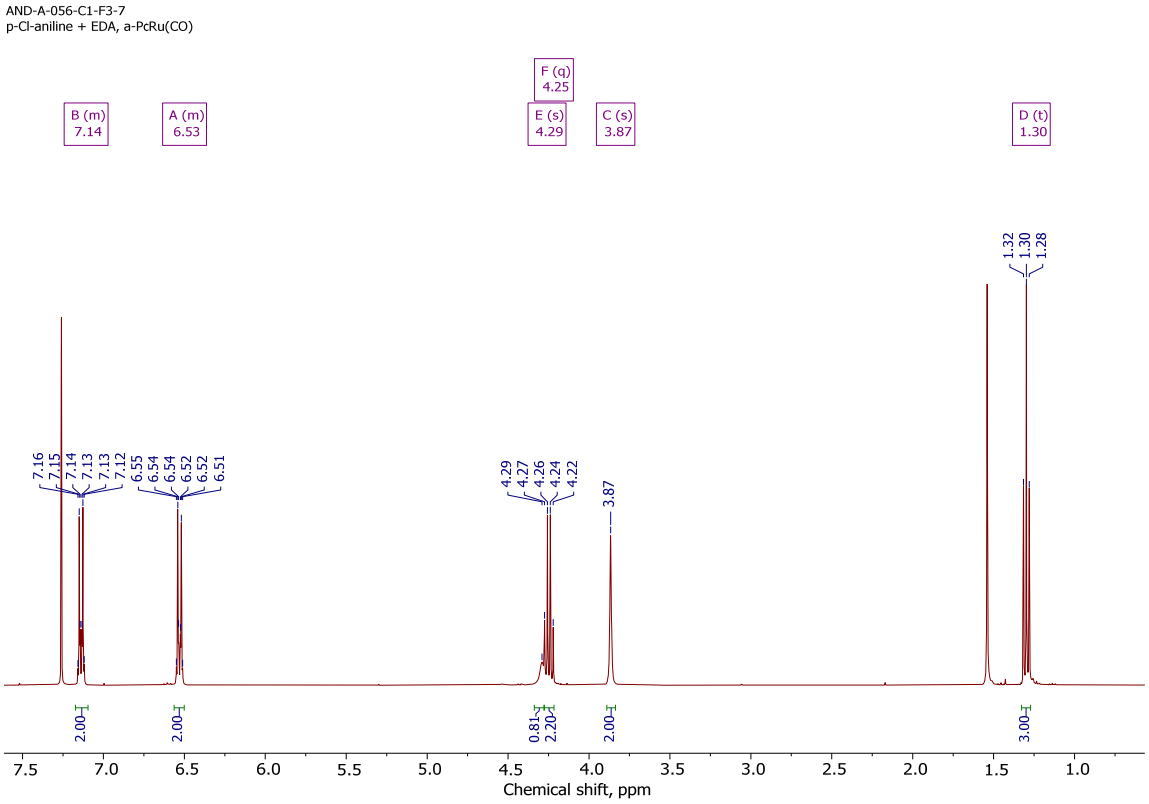


Figure S40. ^{1}H NMR spectrum of ethyl (4-chlorophenyl)glycinate **3e**.

MS (EI) m/z (%): 215 (5.0), 213 (15.5), 142 (32.0), 141 (8.8), 140 (100), 138 (7.7), 111 (10.0), 105 (6.2), 77 (7.0), 75 (9.1).

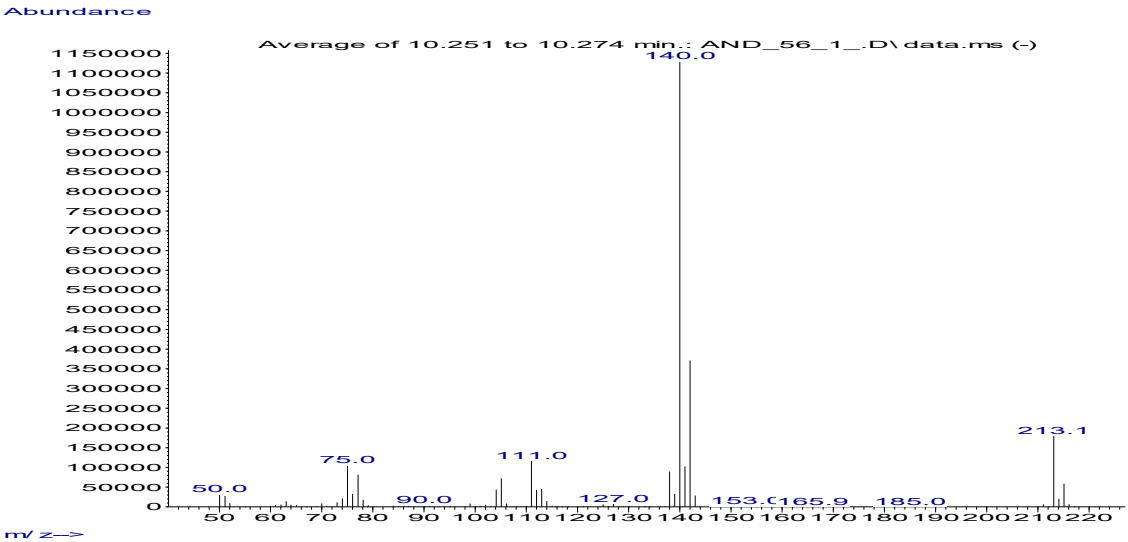


Figure S41. Mass spectrum (EI) of ethyl (4-chlorophenyl)glycinate **3e**.

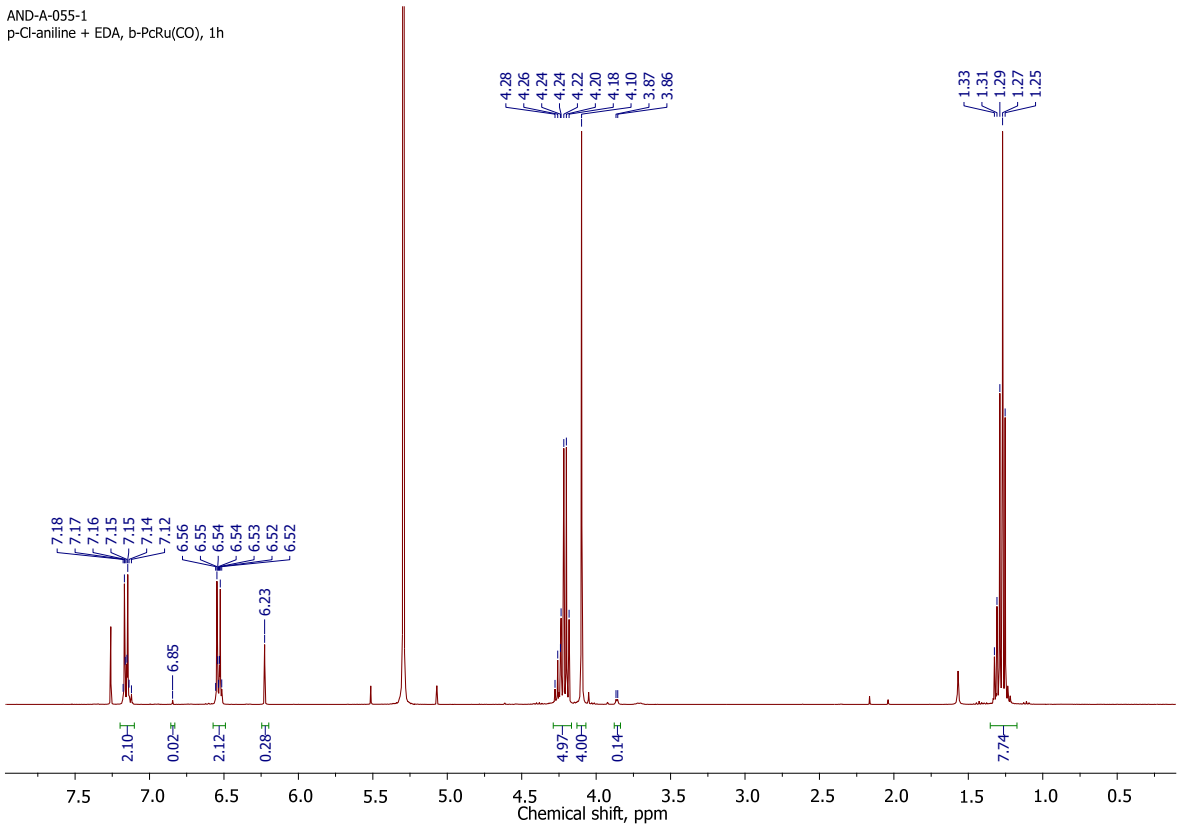


Figure S42. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 4-chloroaniline **2e** in the presence of 0.05 mol. % **1β**.

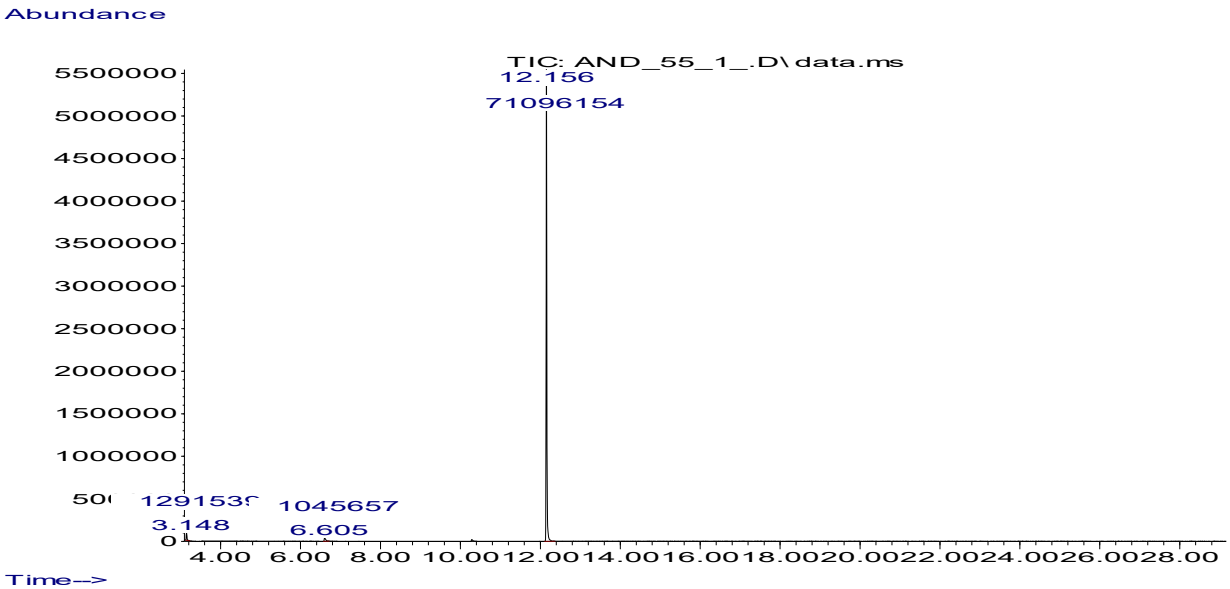
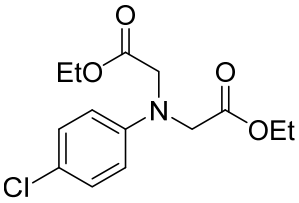


Figure S43. Chromatogram of the reaction mixture after reaction of EDA with 4-chloroaniline **2e** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((4-chlorophenyl)azanediyl)diacetate 4e



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.20 – 7.11 (m, 2H), 6.57 – 6.51 (m, 2H), 4.21 (q, J = 7.1 Hz, 4H), 4.10 (s, 4H), 1.27 (t, J = 7.1 Hz, 6H).

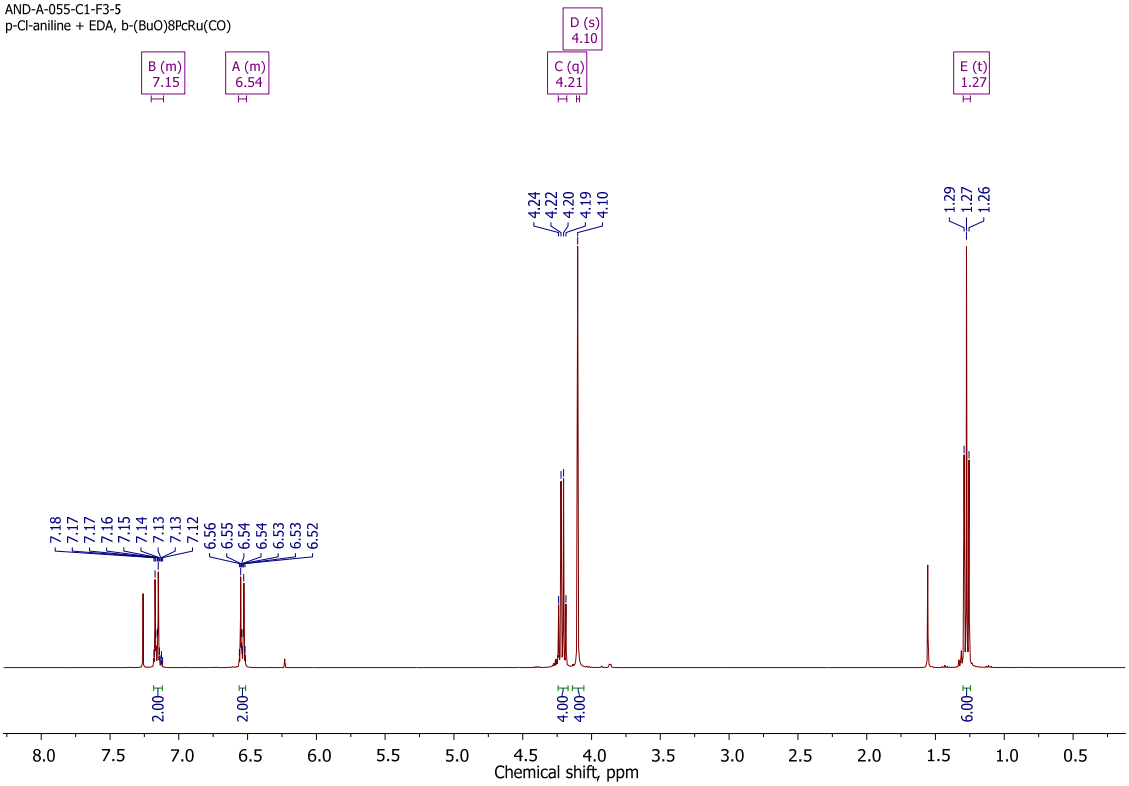


Figure S44. ^{1}H NMR spectrum of diethyl 2,2'-((4-chlorophenyl)azanediyl)diacetate **4e**.

MS (EI) m/z (%): 226 (100), 59 (43.1), 140 (34.1), 228 (33.4), 125 (21.9), 138 (17.4), 299 (17.2), 154 (15.3), 227 (12.8), 111 (12.6).

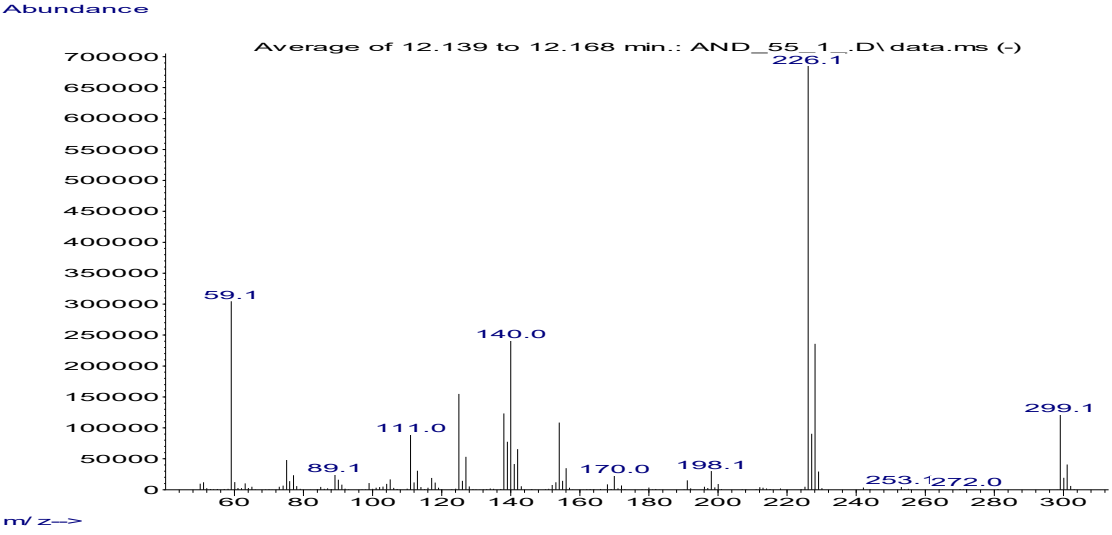


Figure S45. Mass spectrum (EI) of diethyl 2,2'-((4-chlorophenyl)azanediyl)diacetate **4e**.

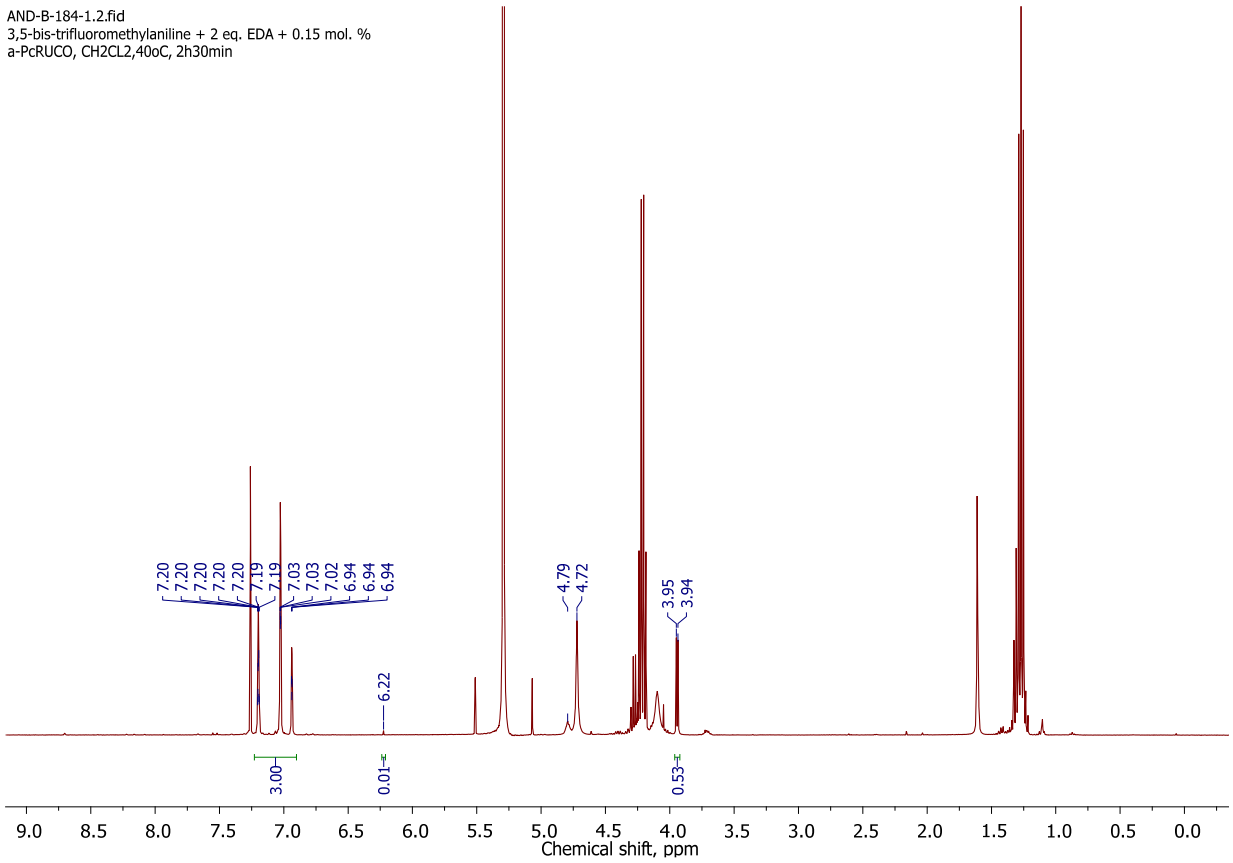


Figure S46. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 3,5-*bis*(trifluoromethyl)aniline **2f** in the presence of 0.15 mol. % **1α**. Reaction time: 2.5 h.

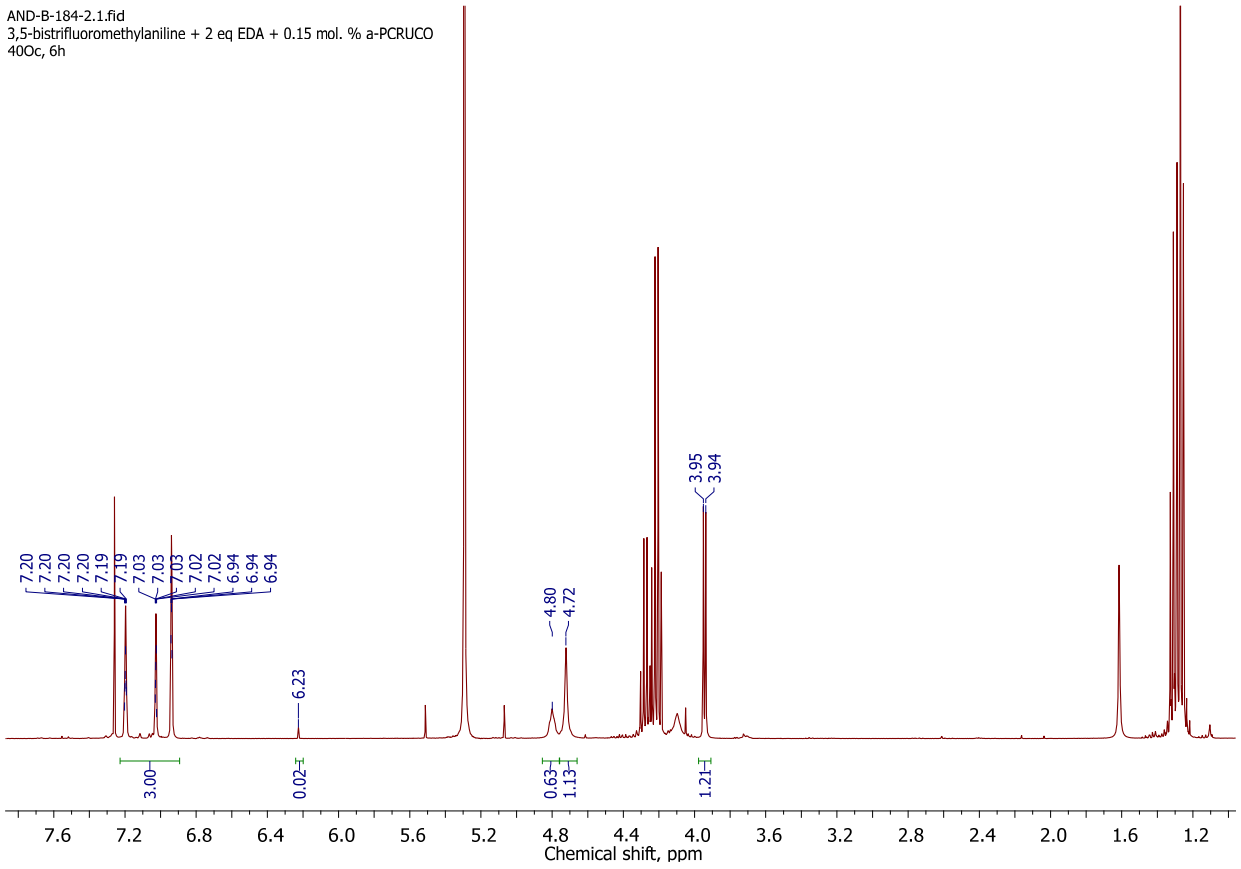


Figure S47. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 3,5-*bis*(trifluoromethyl)aniline **2f** in the presence of 0.15 mol. % **1α**. Reaction time: 6 h.

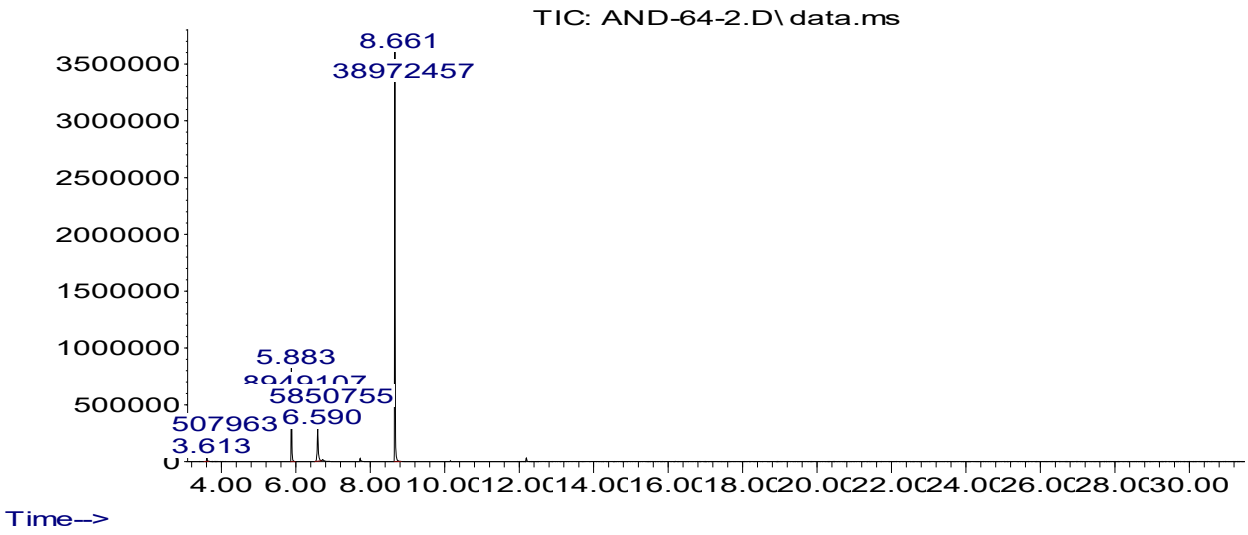
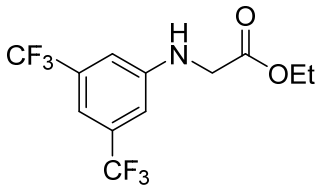


Figure S48. Chromatogram of the reaction mixture after reaction of EDA with 3,5-*bis*(trifluoromethyl)-aniline **2f** in the presence of 0.15 mol. % **1α**. Reaction time: 3 h.

Ethyl (3,5-bis(trifluoromethyl)phenyl)glycinate, 3f



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.20 (s, 1H), 6.94 (s, 2H), 4.79 (br. s., 1H), 4.28 (d, J = 7.1 Hz, 2H), 3.95 (d, J = 5.1 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H).

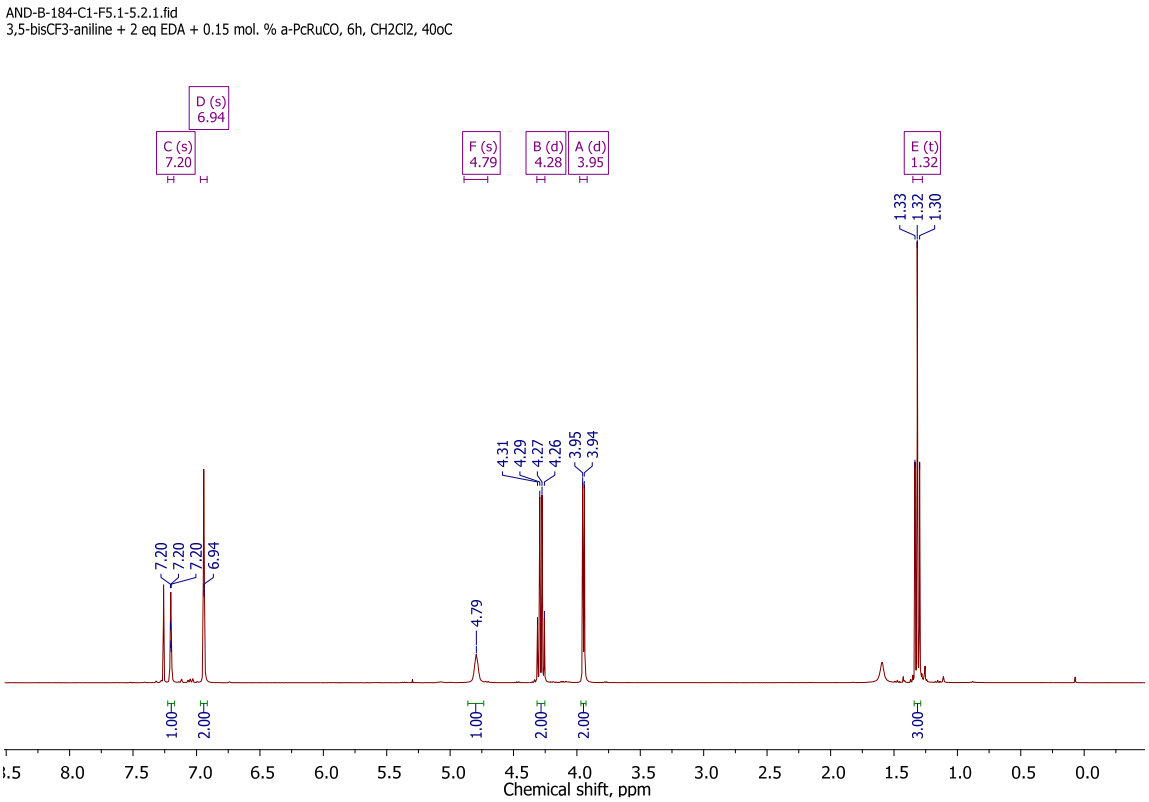


Figure S49. ^{1}H NMR spectrum of ethyl (3,5-*bis*(trifluoromethyl)phenyl)glycinate **3f**.

MS (EI) m/z (%): 315 (8.0), 296 (5.9), 243 (10.4), 242 (100), 240 (6.0), 213 (5.6), 195 (4.8), 194 (3.2), 163 (3.2), 144 (3.0)

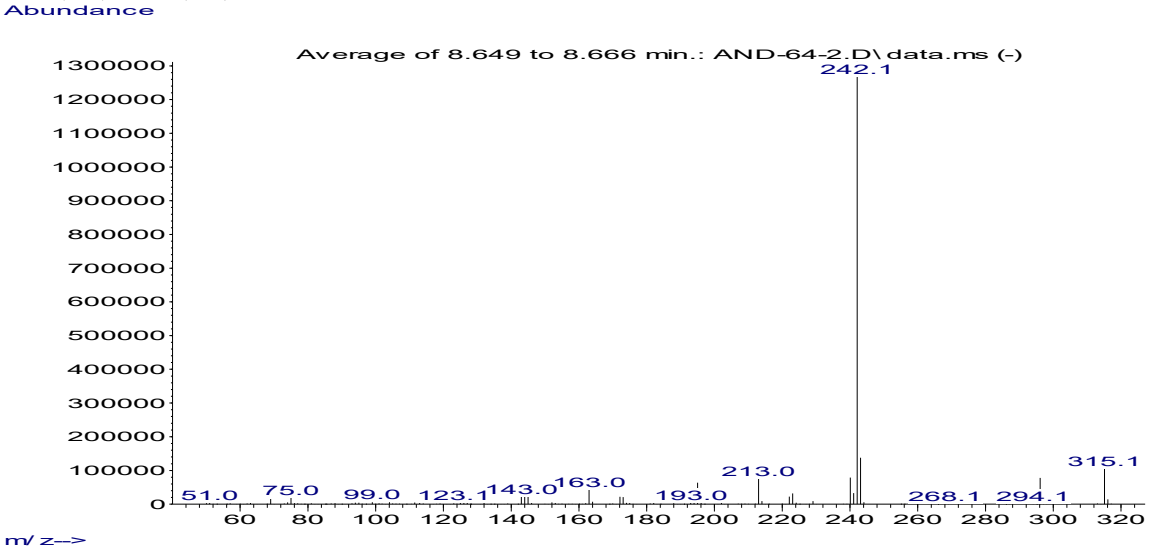


Figure S50. Mass spectrum (EI) of ethyl (3,5-*bis*(trifluoromethyl)phenyl)glycinate **3f**.

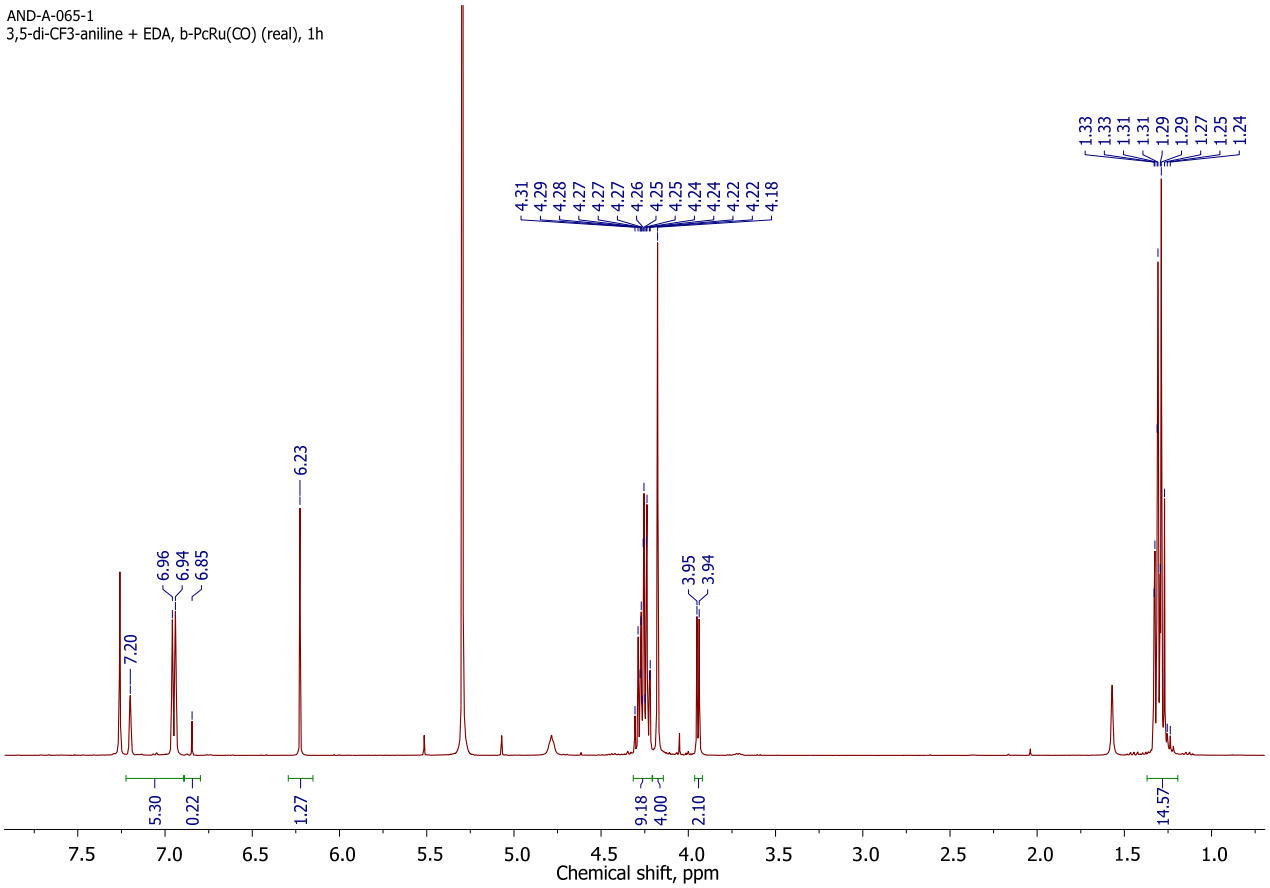


Figure S51. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 3,5-*bis*(trifluoro-methyl)aniline **2f** in the presence of 0.05 mol. % **1β**.

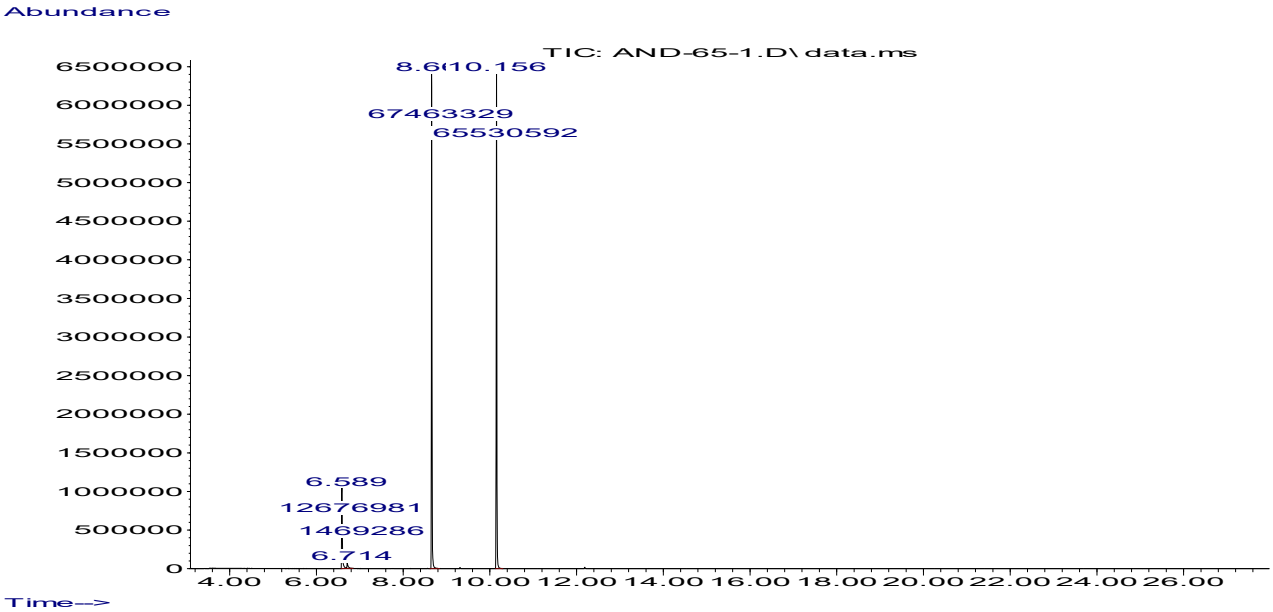
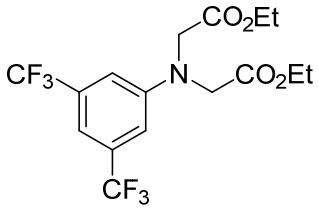


Figure S52. Chromatogram of the reaction mixture after reaction of 3,5-*bis*(trifluoromethyl)aniline **2f** with EDA in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((3,5-bis(trifluoromethyl)phenyl)azanediyl)diacetate, 4f



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.96 (s, 2H), 4.25 (q, J = 7.1 Hz, 4H), 4.18 (s, 4H), 1.29 (t, J = 7.1 Hz, 6H).

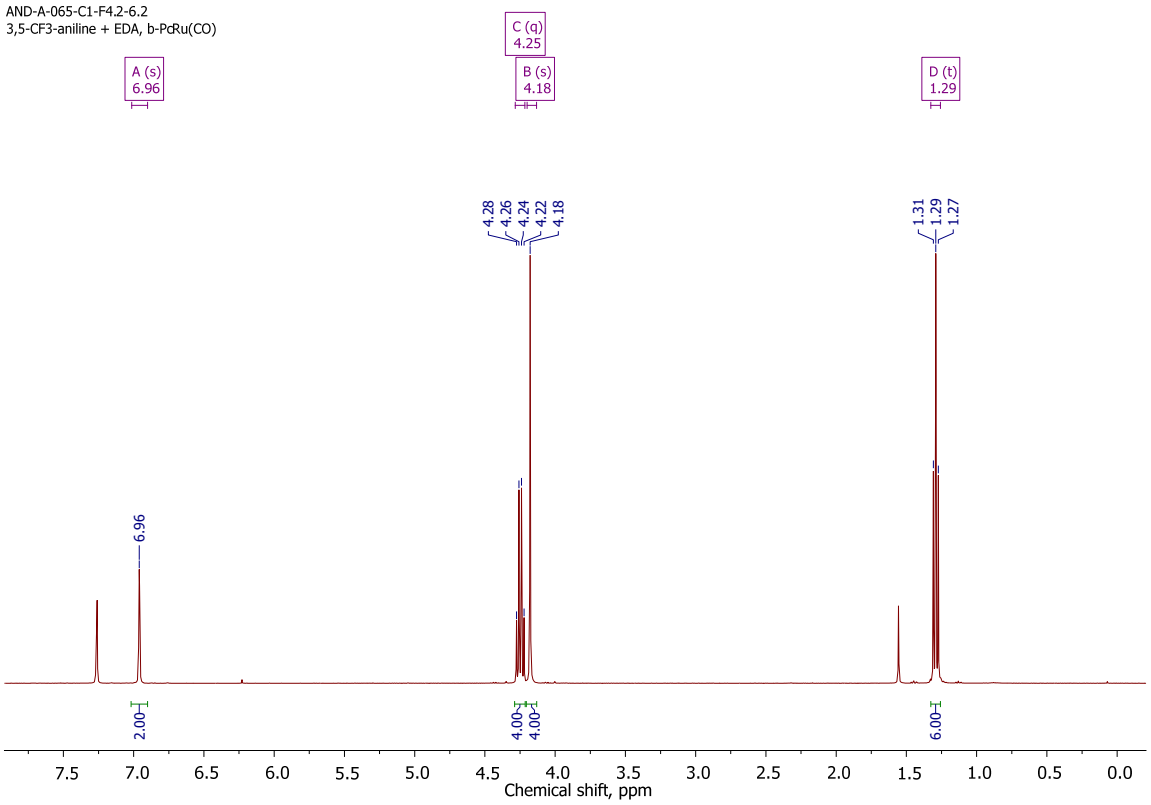


Figure S53. ^{1}H NMR spectrum of diethyl 2,2'-((3,5-*bis*(trifluoromethyl)phenyl)azanediyl)diacetate **4f**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 169.53, 148.60, 132.53 (q, J = 32.8 Hz), 123.45 (q, J = 272.7 Hz), 112.16 – 111.73 (m), 111.40 (hept, J = 4.0 Hz), 61.61, 53.44, 14.06.

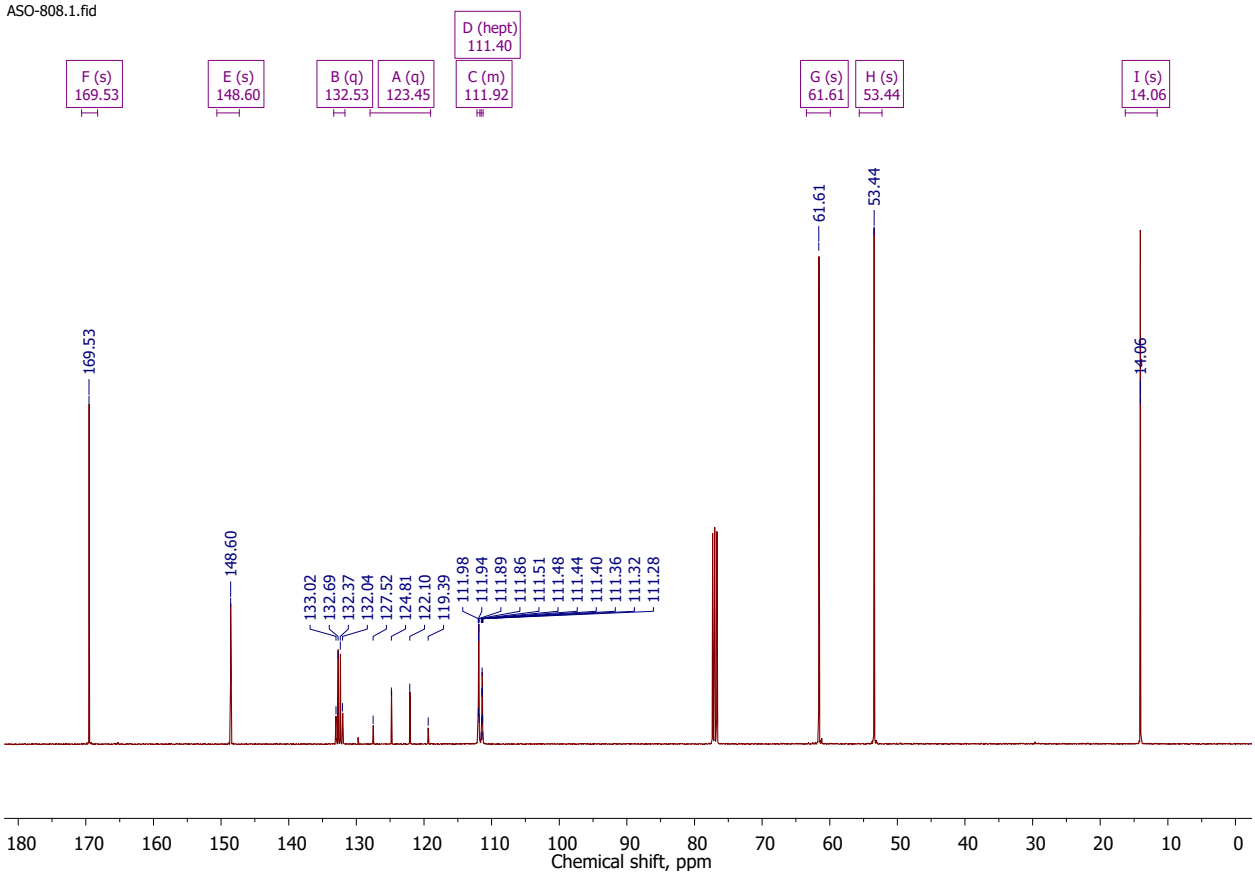


Figure S54. ^{13}C NMR spectrum of diethyl 2,2'-((3,5-*bis*(trifluoromethyl)phenyl)azanediyl)diacetate **4f**.

^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm): -63.24.

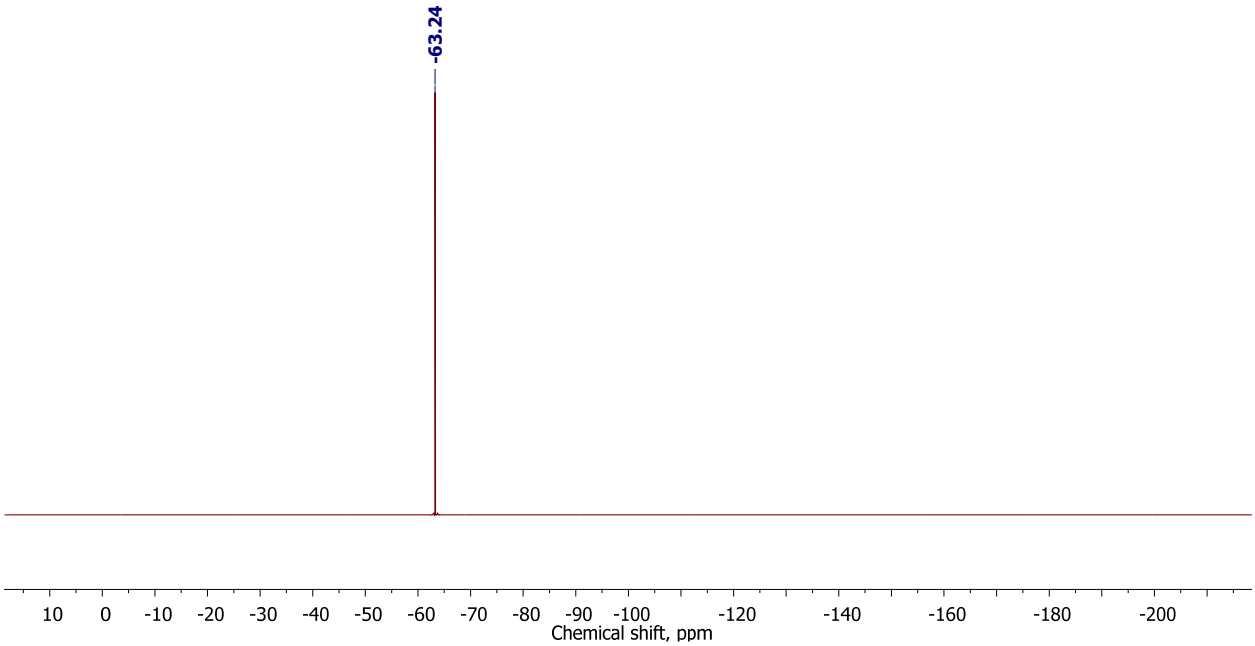


Figure S55. ^{19}F NMR spectrum of diethyl 2,2'-((3,5-*bis*(trifluoromethyl)phenyl)azanediyl)diacetate **4f**.

MS (EI) m/z (%): 401 (10.9), 382 (10.5), 329 (14.9), 328 (100), 242 (46.1), 240 (13.3), 227 (34.3), 222 (7.4), 213 (12.6), 59 (73.1).

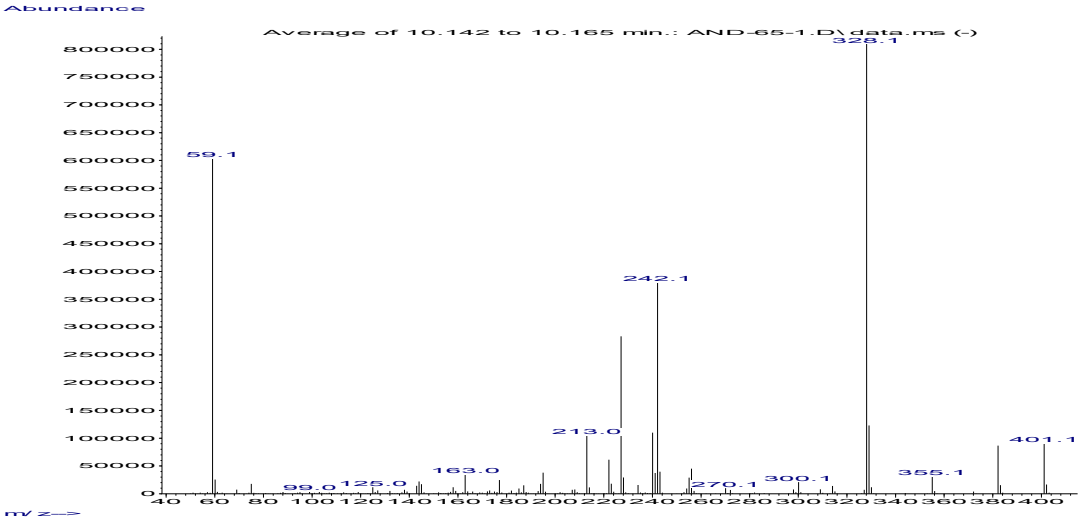


Figure S56. Mass spectrum (EI) of diethyl 2,2'-((3,5-*bis*(trifluoromethyl)phenyl)azanediyl)diacetate **4f**.

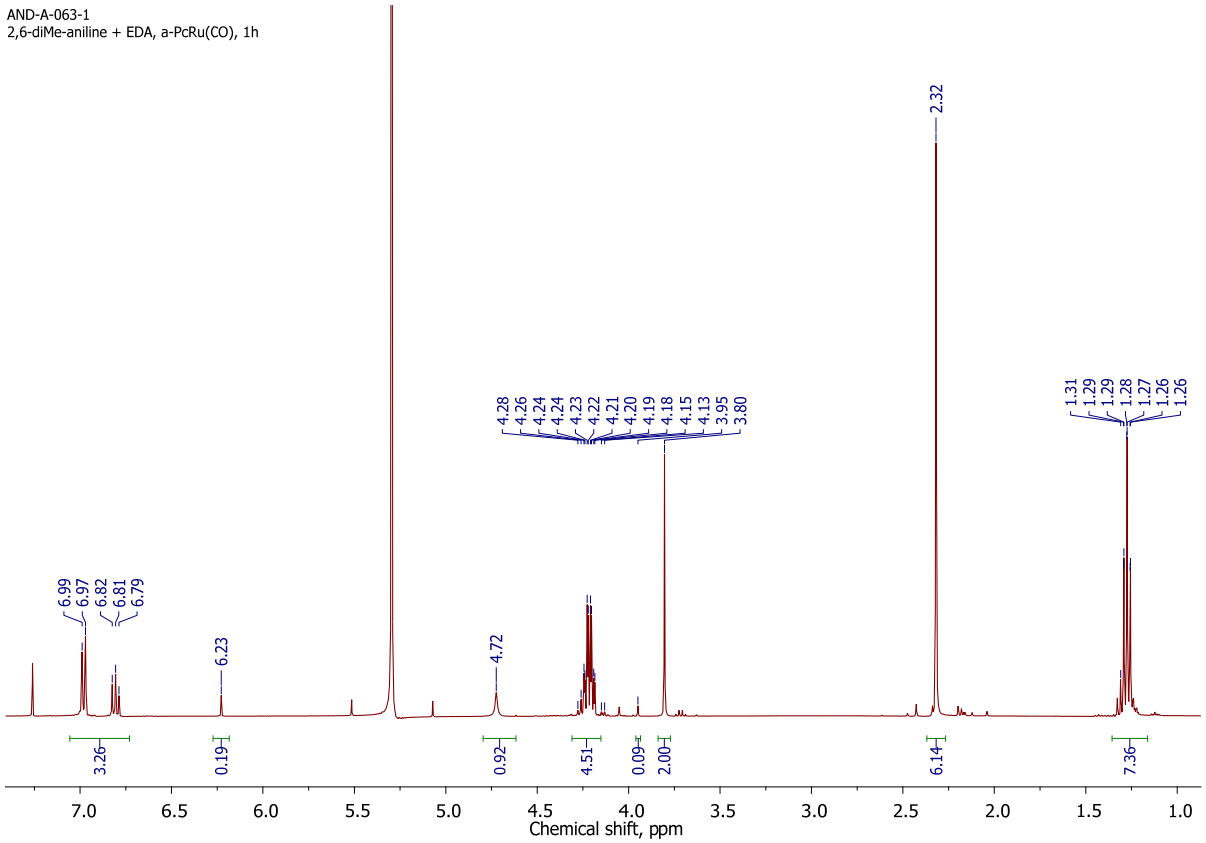


Figure S57. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 2,6-dimethylaniline **2g** in the presence of 0.15 mol. % **1α**.

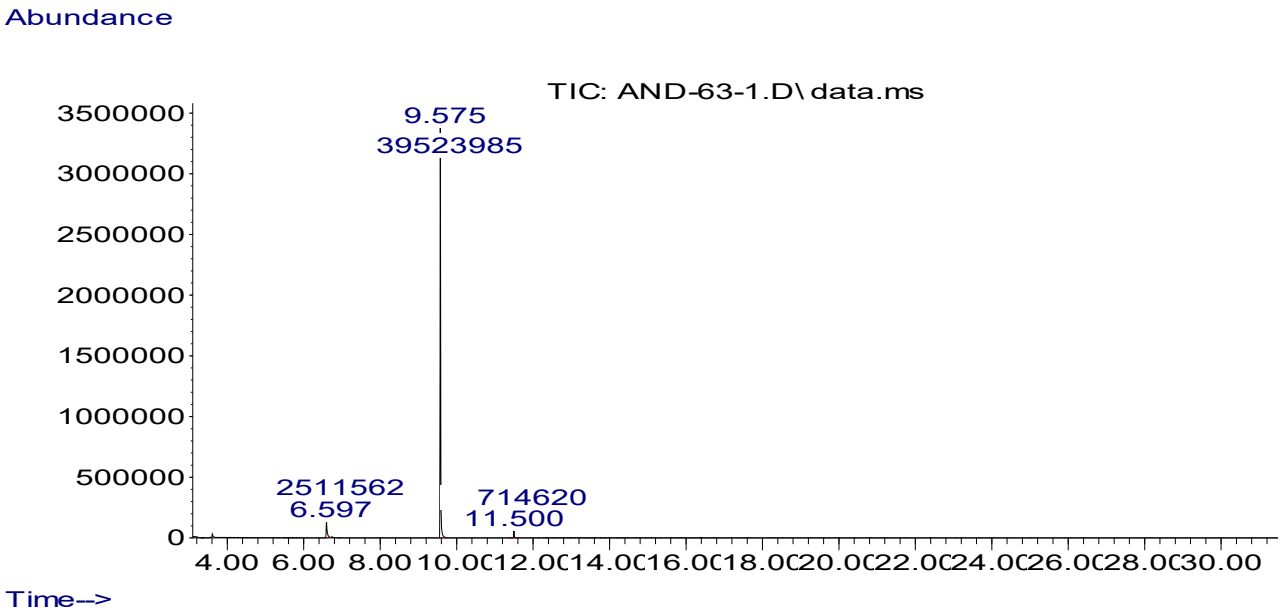
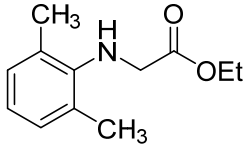


Figure S58. Chromatogram of the reaction mixture after reaction of EDA with 2,6-dimethylaniline **2g** in the presence of 0.15 mol. % **1α**.

Ethyl (2,6-dimethylphenyl)glycinate, 3g



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.91 (d, J = 7.4 Hz, 2H), 6.74 (t, J = 7.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.87 (s, 1H), 3.73 (s, 2H), 2.25 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H).

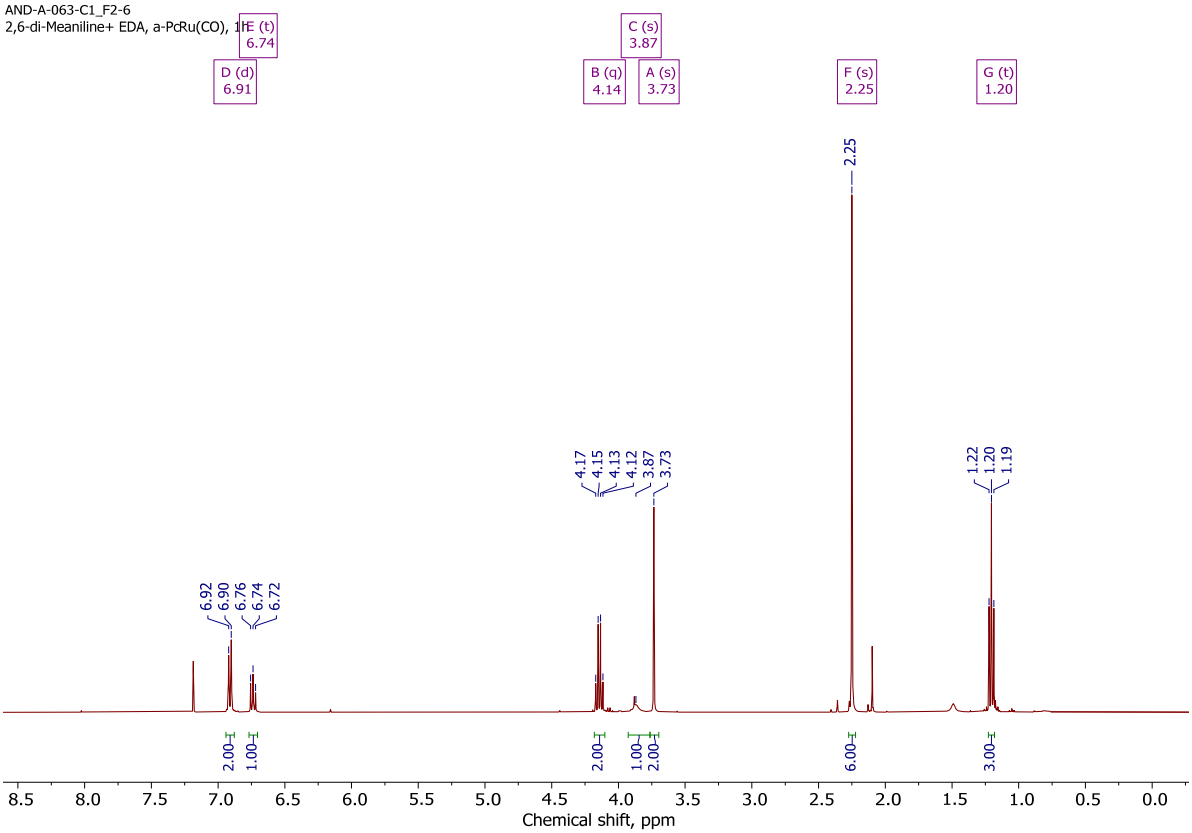


Figure S59. ^{1}H NMR spectrum of ethyl (2,6-dimethylphenyl)glycinate **3g**.

MS (EI) m/z (%): 207 (16.2), 135 (10.4), 134 (100), 132 (9.2), 117 (5.3),105 (11.1), 103 (4.6), 91 (3.7), 79 (6.2), 77 (8.2).

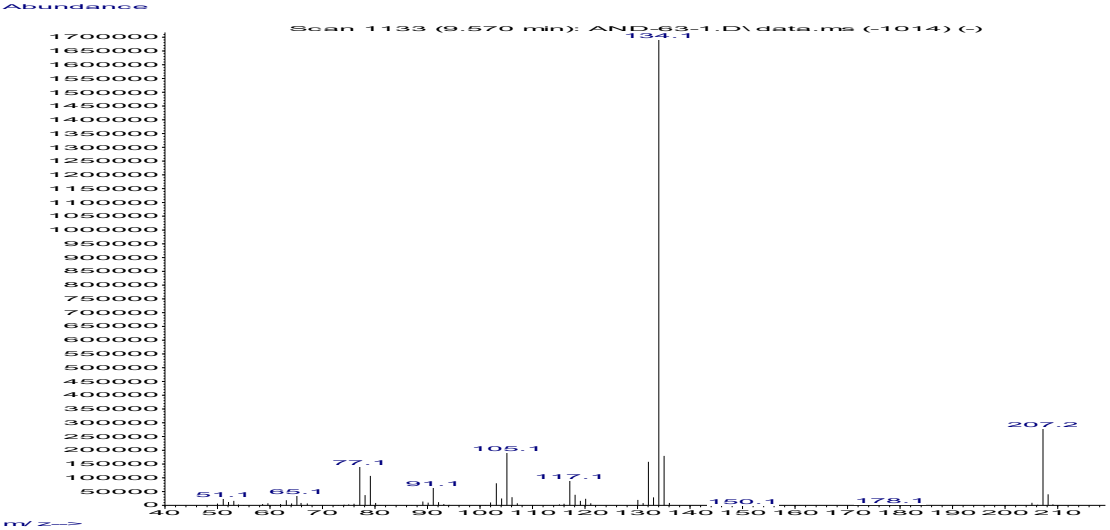


Figure S60. Mass spectrum (EI) of ethyl (2,6-dimethylphenyl)glycinate **3g**.

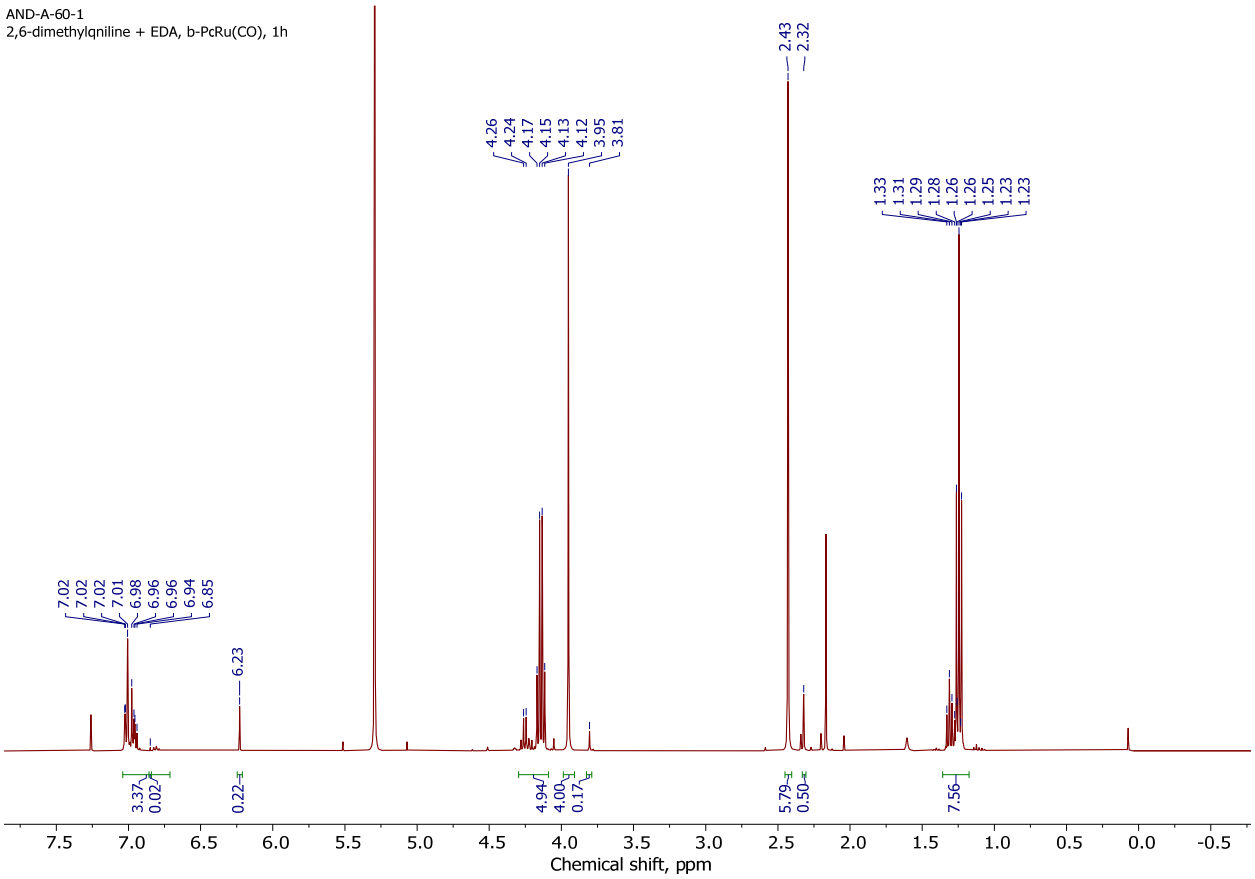


Figure S61. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 2,6-dimethylaniline **2g** in the presence of 0.05 mol. % **1β**.

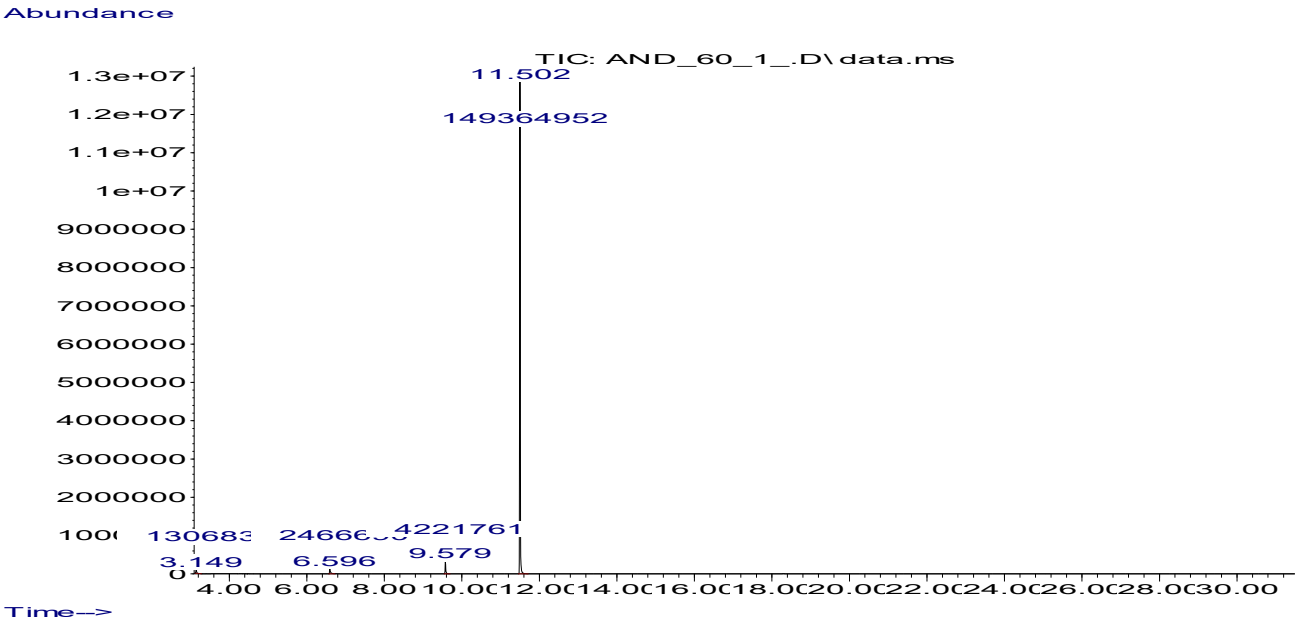
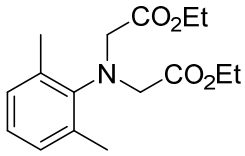


Figure S62. Chromatogram of the reaction mixture after reaction of EDA with 2,6-dimethylaniline **2g** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((2,6-dimethylphenyl)azanediyl)diacetate, 4g



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.03 – 6.94 (m, 3H), 4.14 (q, J = 7.1 Hz, 4H), 3.95 (s, 4H), 3.81 (s, 1H), 2.43 (s, 6H), 1.25 (t, J = 7.1 Hz, 6H).

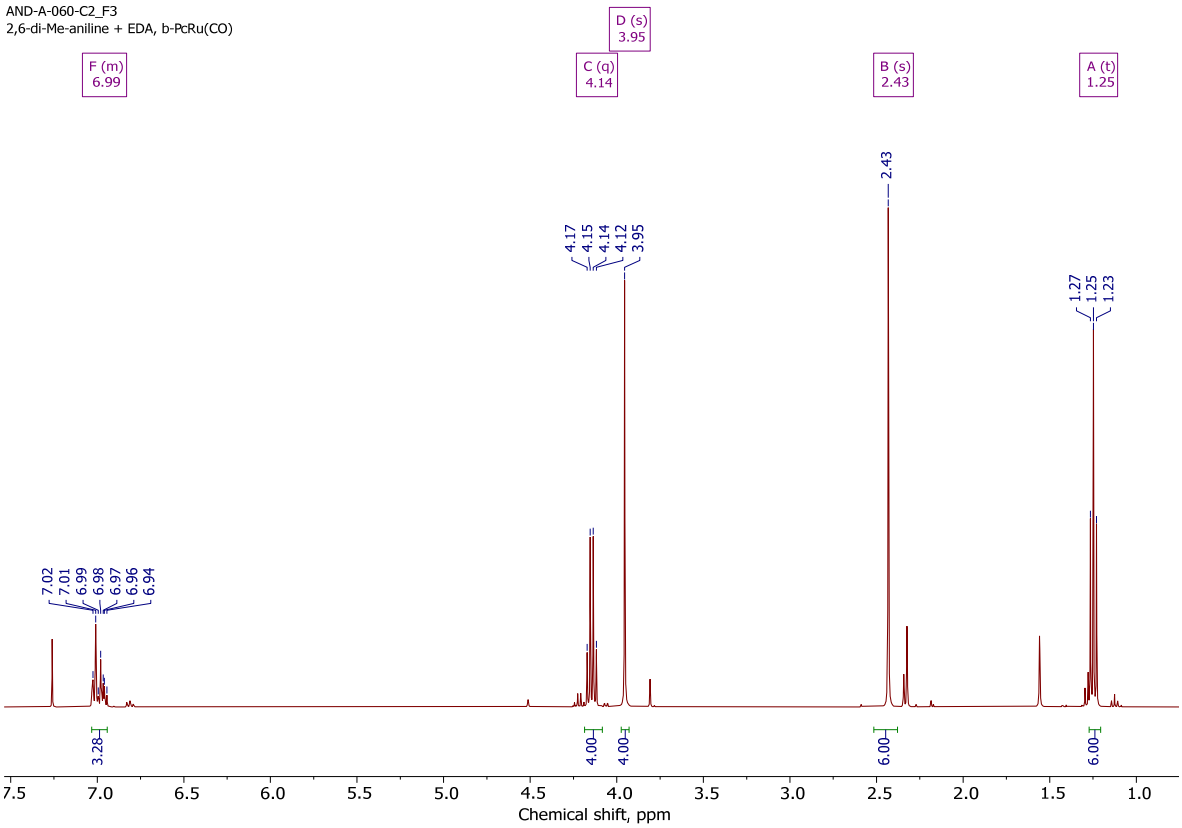


Figure S63. ^{1}H NMR spectrum of diethyl 2,2'-((2,6-dimethylphenyl)azanediyl)diacetate **4g**.

MS (EI) m/z (%): 293 (8.4), 221 (15.8), 220 (100), 192 (12.4), 146 (17.1), 134 (11.1), 132 (21.3), 117 (7.9), 77 (6.9), 59 (8.4).

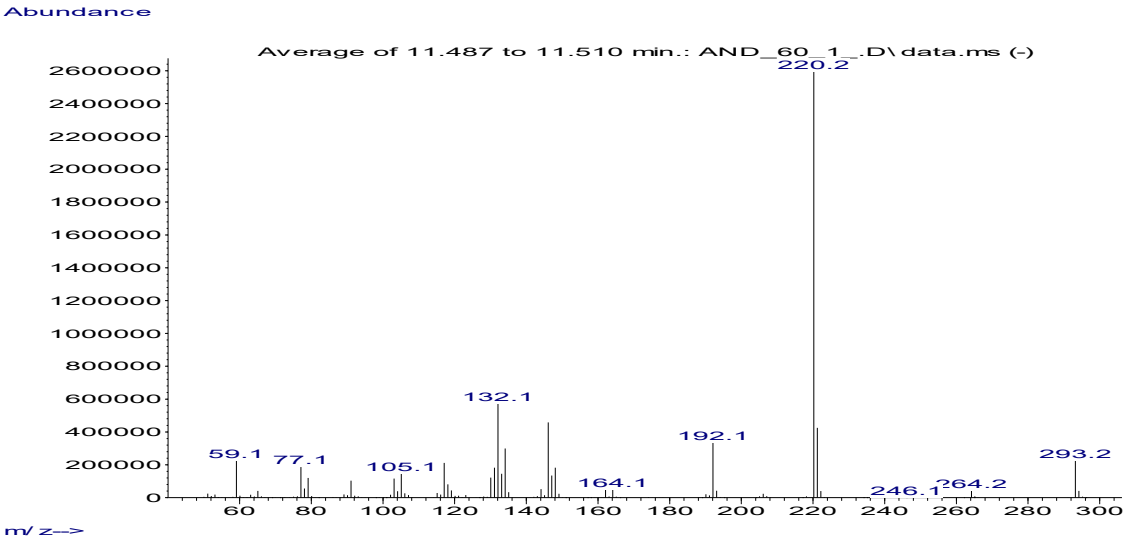


Figure S64. Mass spectrum (EI) of diethyl 2,2'-((2,6-dimethylphenyl)azanediyl)diacetate **4g**.

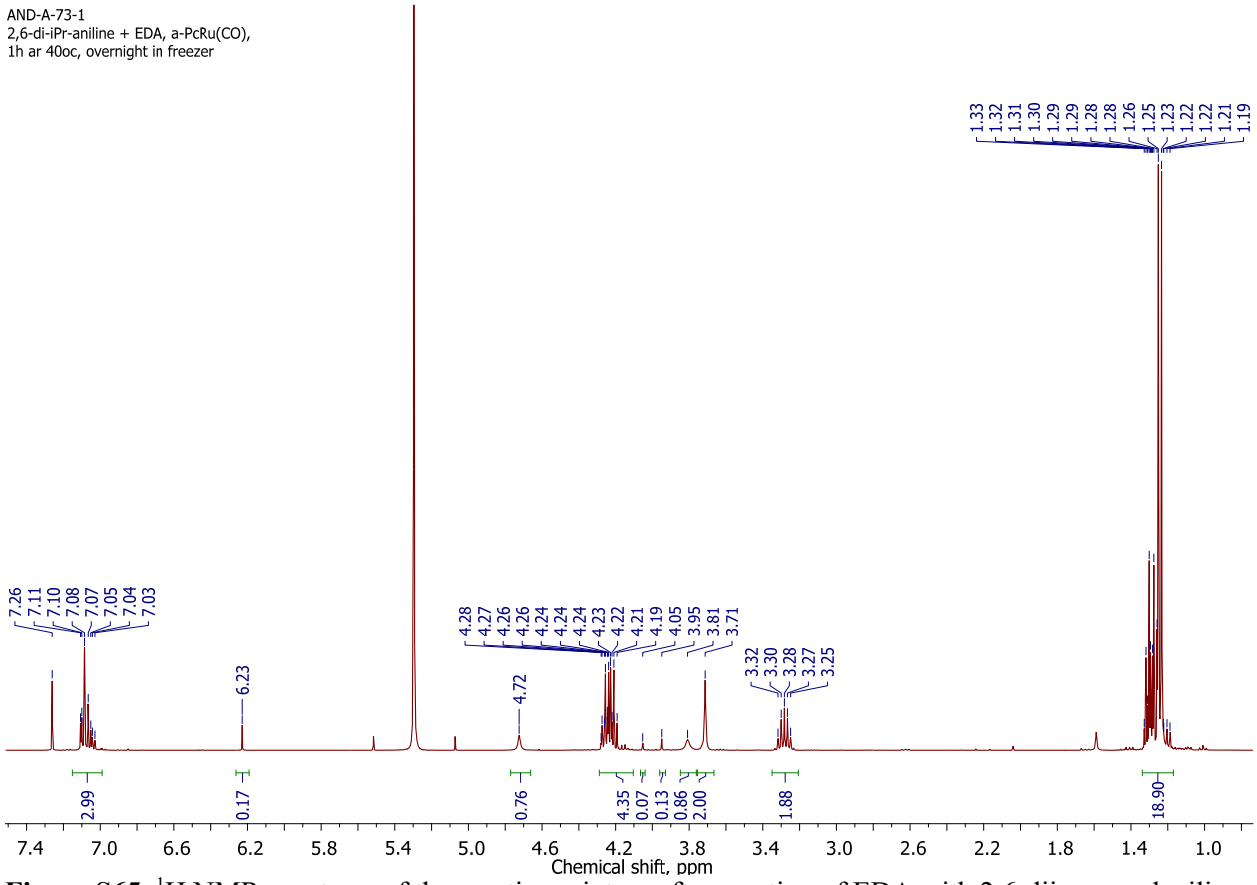
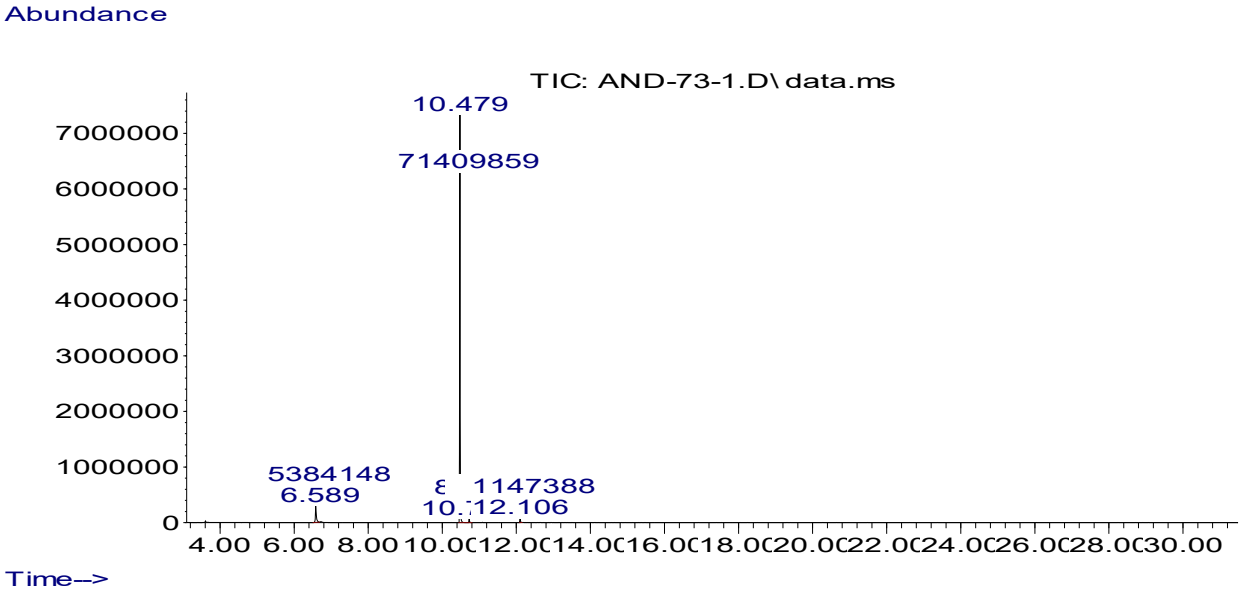
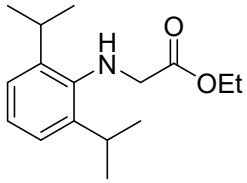


Figure S65. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 2,6-diisopropylaniline **2h** in the presence of 0.15 mol. % **1α**.



Ethyl (2,6-diisopropylphenyl)glycinate, 3h



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.12 – 7.04 (m, 3H), 4.26 (q, J = 7.1 Hz, 2H), 3.83 (s, 1H), 3.73 (s, 2H), 3.30 (hept, J = 6.8 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.26 (d, J = 6.9 Hz, 12H).

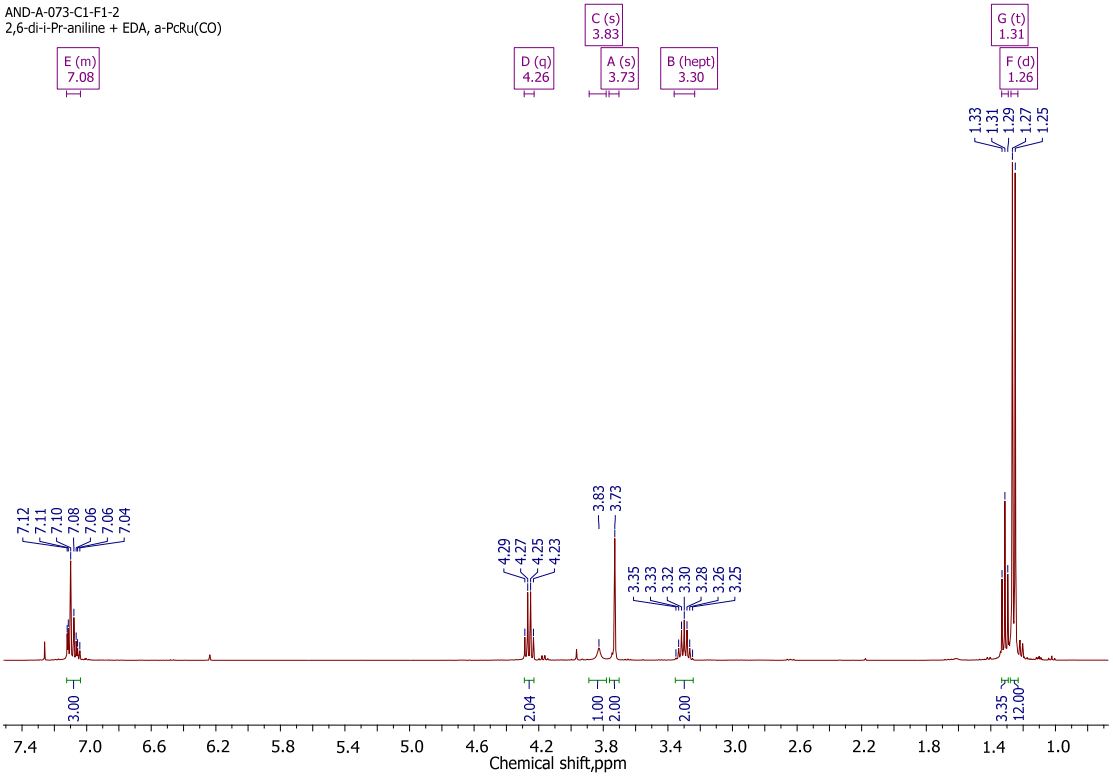


Figure S67. ^{1}H NMR spectrum of ethyl (2,6-diisopropylphenyl)glycinate **3h**.

MS (EI) m/z (%): 263 (23.8), 191 (14.9), 190 (100), 176 (22.0), 175 (20.3), 160 (21.6), 146 (15.5), 132 (13.0), 130 (8.5), 117 (7.6).

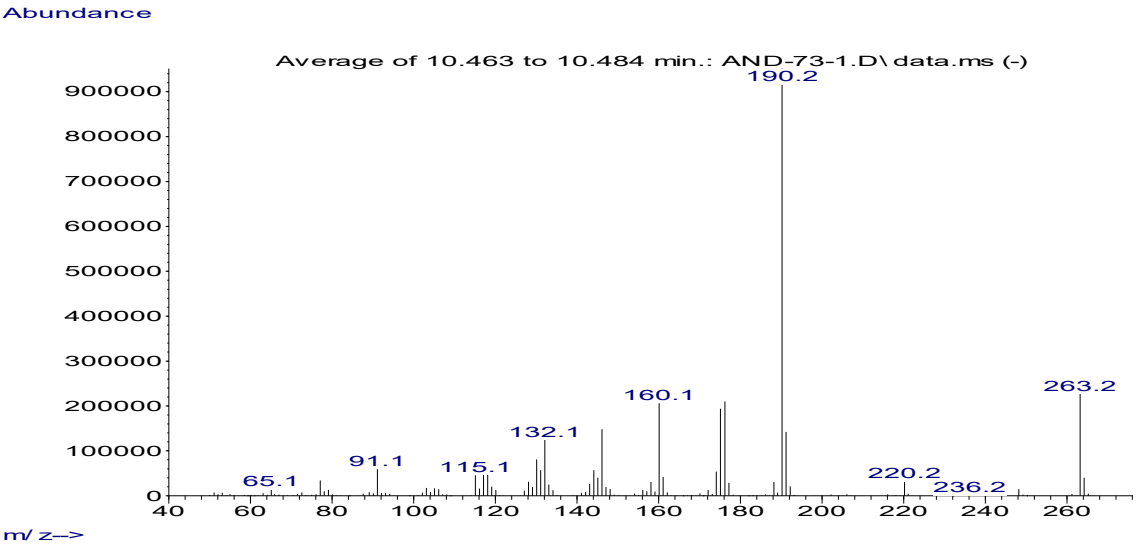


Figure S68. Mass spectrum (EI) of ethyl (2,6-diisopropylphenyl)glycinate **3h**.

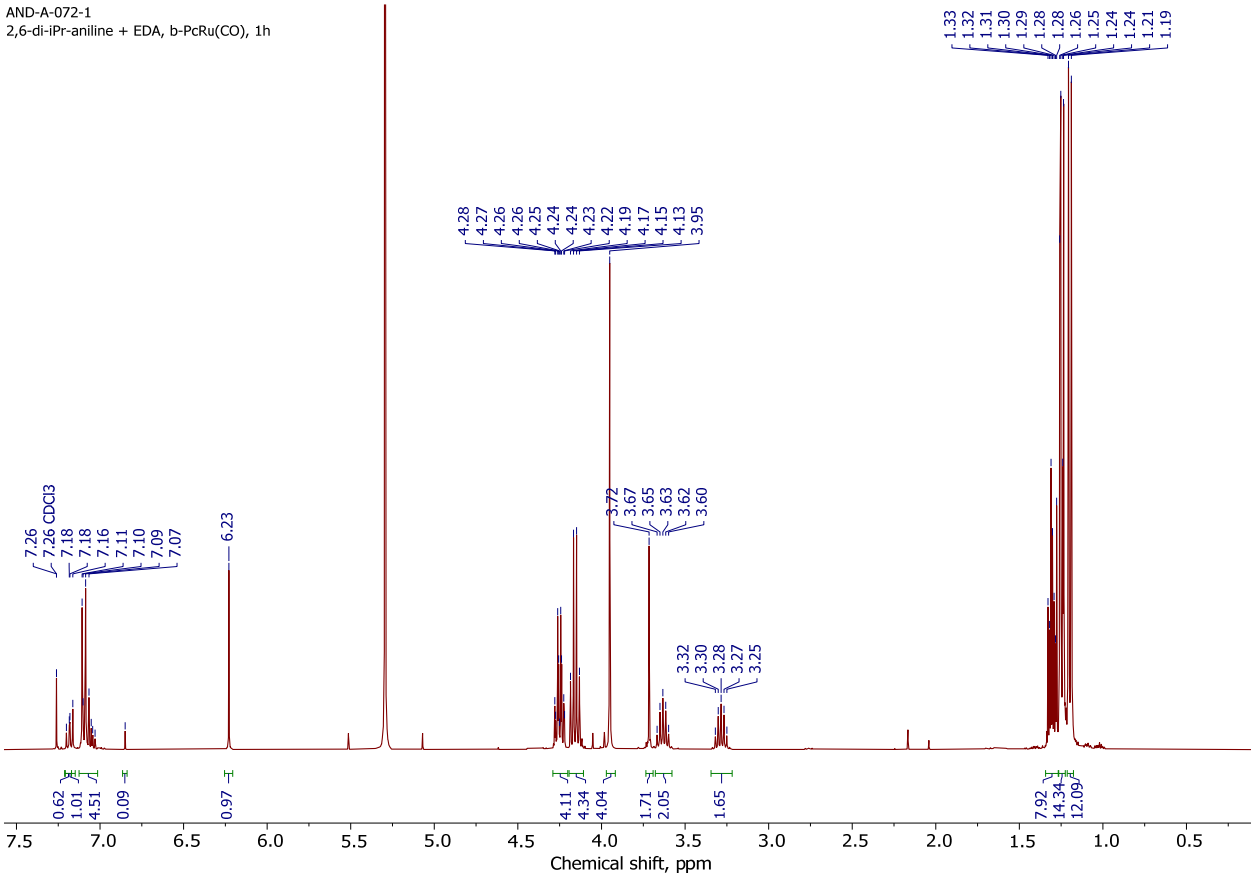


Figure S69. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 2,6-diisopropylaniline **2h** in the presence of 0.05 mol. % **1β**.

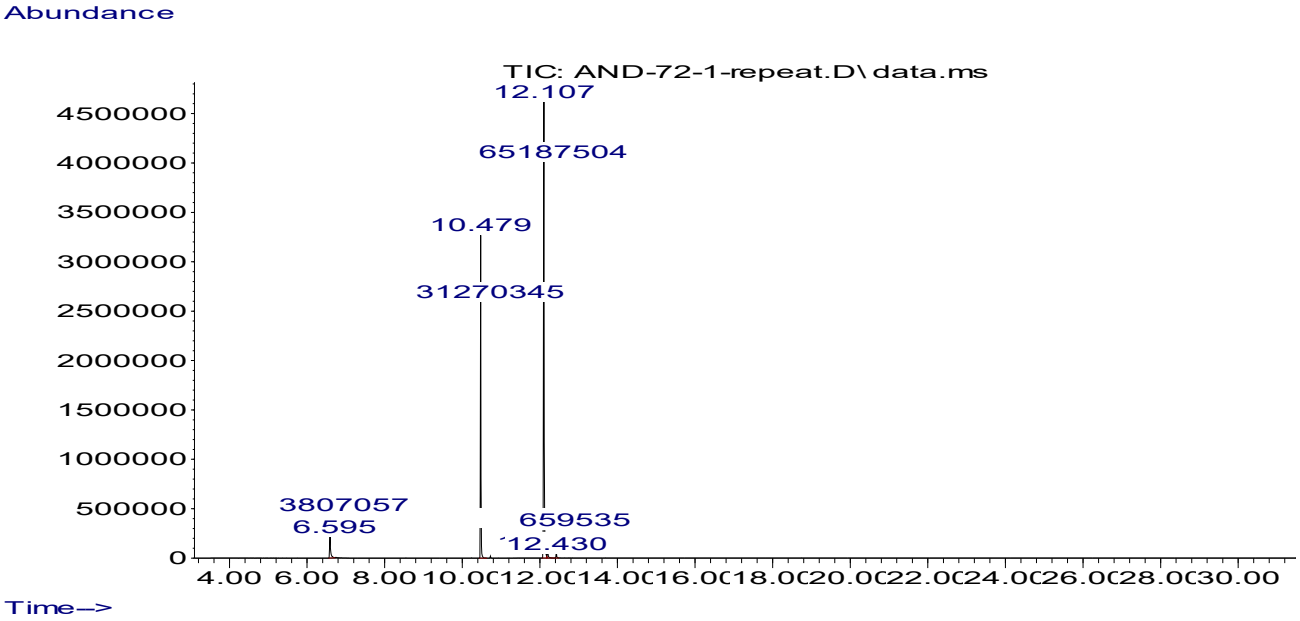
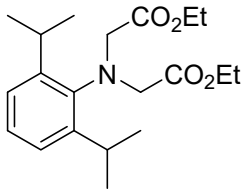


Figure S70. Chromatogram of the reaction mixture after reaction of EDA with 2,6-diisopropylaniline **2h** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((2,6-diisopropylphenyl)azanediyl)diacetate, 4h



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.18 (dd, J = 8.4, 6.8 Hz, 1H), 7.12 – 7.08 (m, 2H), 4.16 (q, J = 7.1 Hz, 4H), 3.95 (s, 4H), 3.63 (hept, J = 6.8 Hz, 2H), 1.26 (t, J = 7.1 Hz, 6H), 1.20 (d, J = 6.9 Hz, 12H).

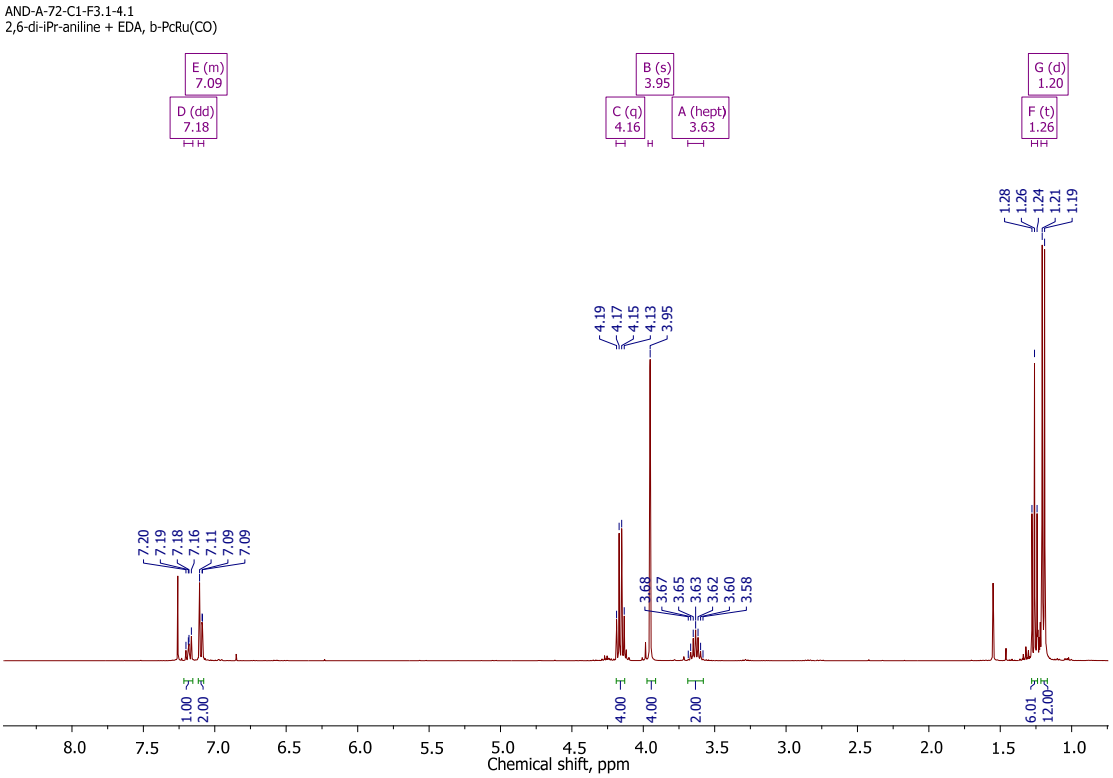


Figure S71. ^{1}H NMR spectrum of diethyl 2,2'-((2,6-diisopropylphenyl)azanediyl)diacetate **4h**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 171.69, 148.51, 146.00, 126.96, 124.45, 60.48, 56.63, 27.87, 24.72, 14.24.

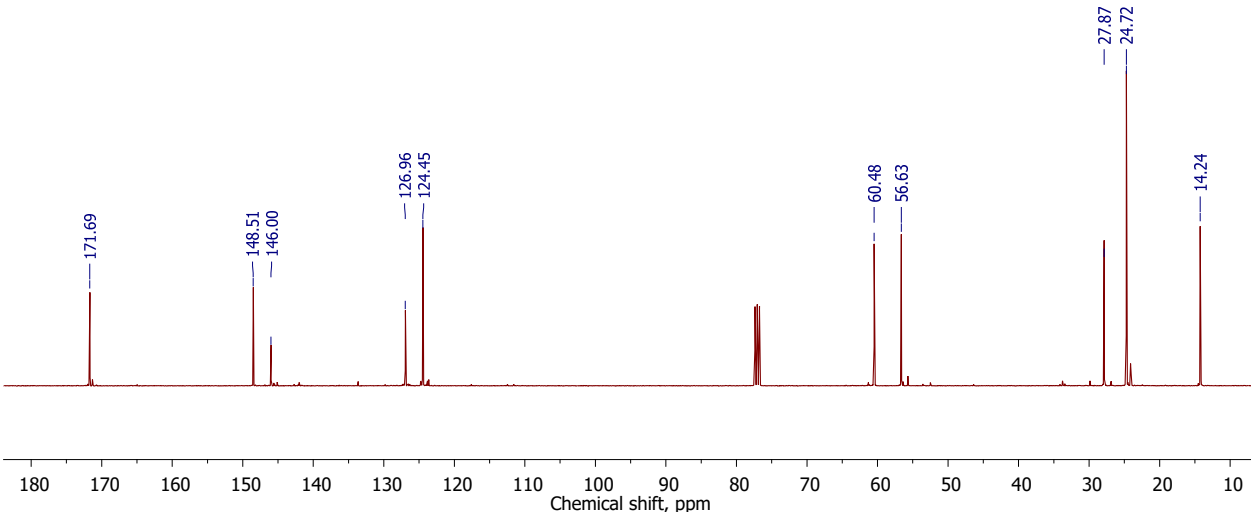


Figure S72. ^{13}C NMR spectrum of diethyl 2,2'-((2,6-diisopropylphenyl)azanediyl)diacetate **4h**.

MS (EI) m/z (%): 349 (5.9), 277 (19.4), 276 (100), 202 (11.0), 174 (6.6), 160 (6.4), 158 (6.7), 146 (10.2), 144 (7.2), 132 (13.5).

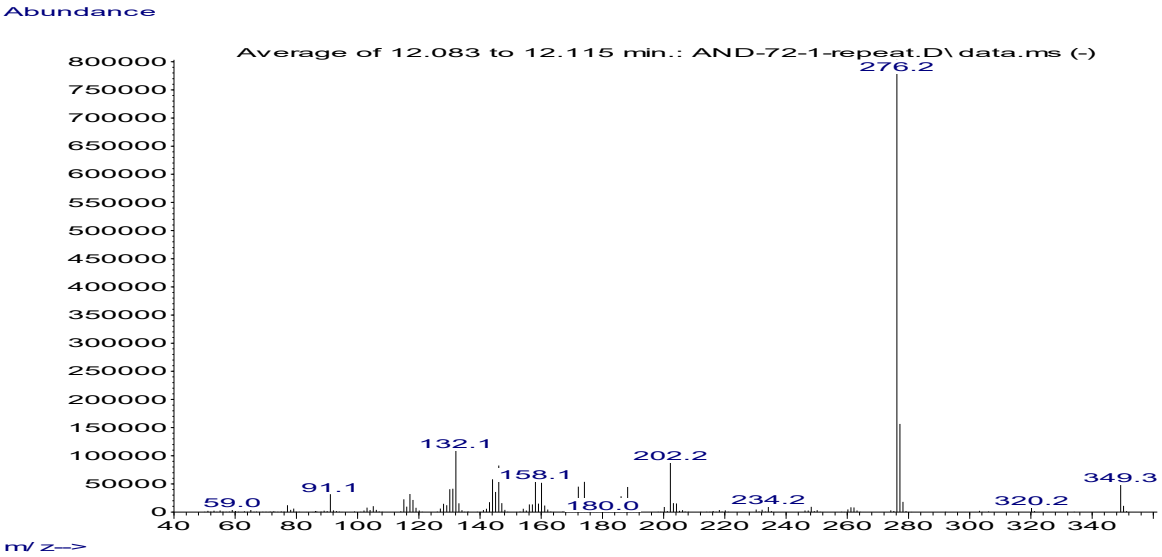


Figure S73. Mass spectrum (EI) of diethyl 2,2'-((2,6-diisopropylphenyl)azanediyl)diacetate **4h**.

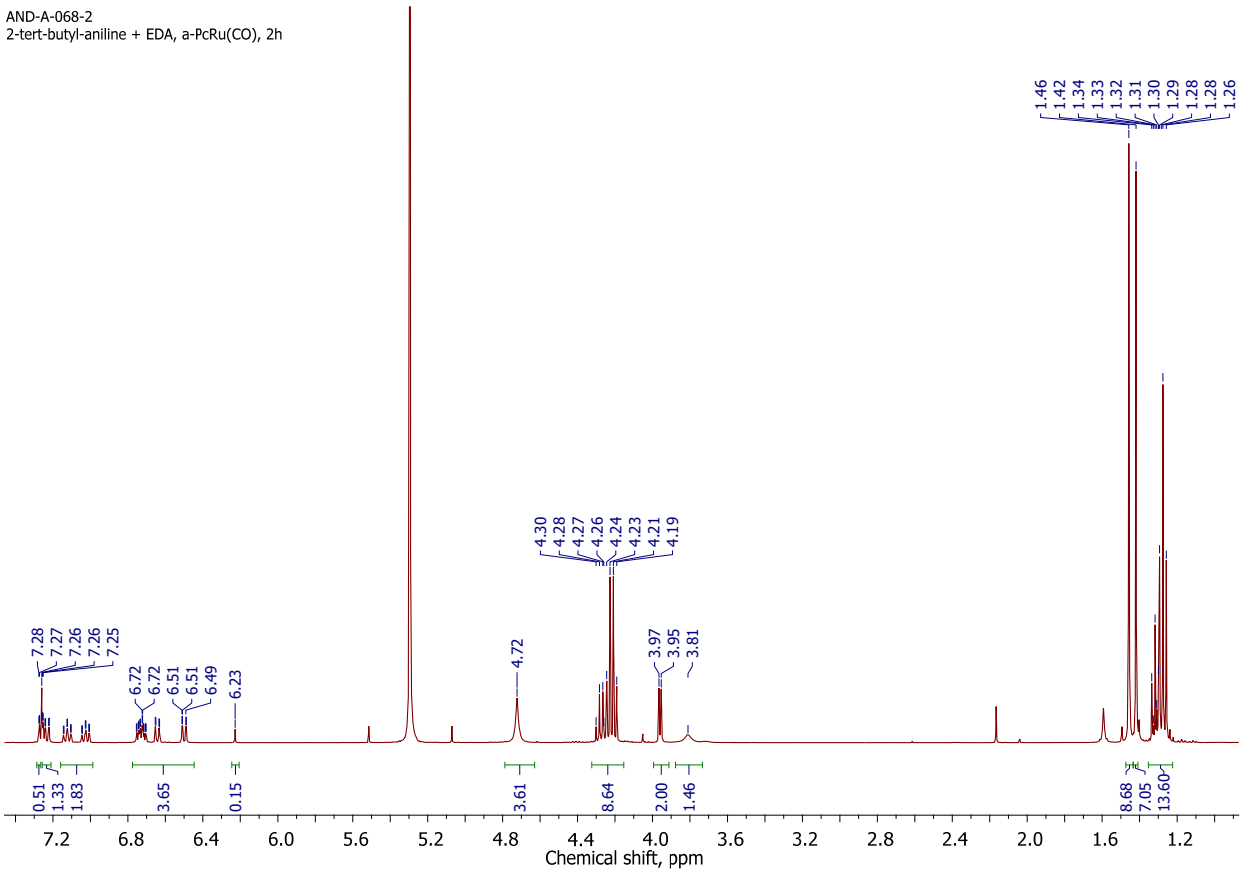


Figure S74. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 2-(*tert*-butyl)aniline **2i** in the presence of 0.15 mol. % **1α**.

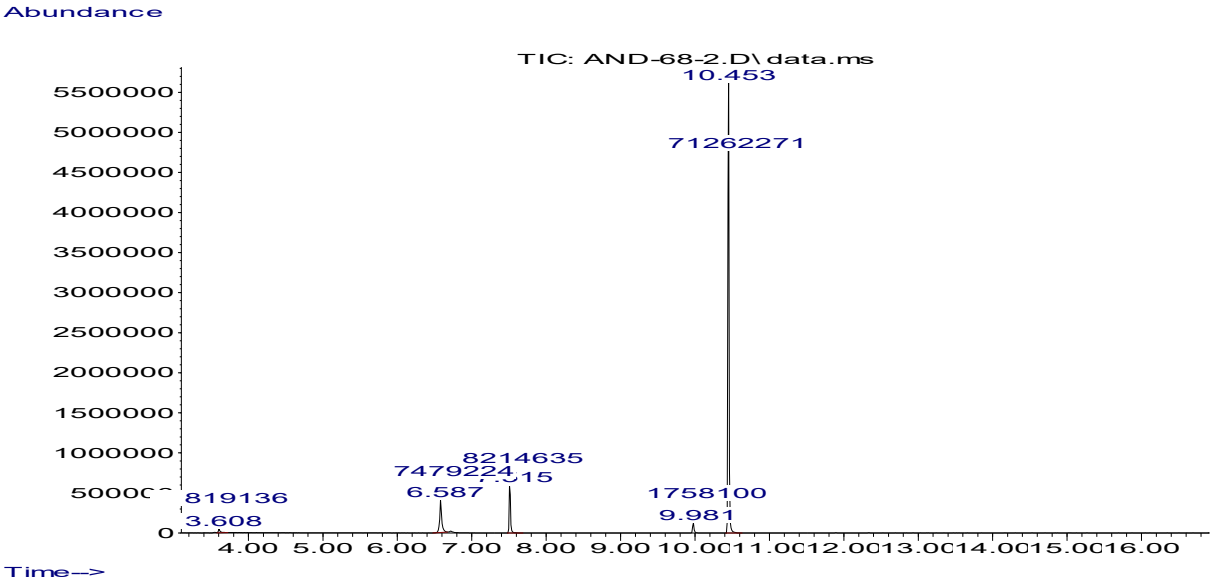
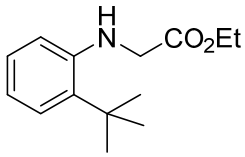


Figure S75. Chromatogram of the reaction mixture after reaction of EDA with 2-(*tert*-butyl)aniline **2i** in the presence of 0.15 mol. % **1α**.

Ethyl (2-(*tert*-butyl)phenyl)glycinate, 3i



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.27 (dd, J = 7.8, 1.4 Hz, 1H), 7.13 (td, J = 8.0, 1.5 Hz, 1H), 6.73 (td, J = 7.7, 1.3 Hz, 1H), 6.51 (dd, J = 8.0, 1.2 Hz, 1H), 4.73 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.97 (d, J = 4.8 Hz, 2H), 1.46 (s, 9H), 1.32 (t, J = 7.1 Hz, 3H).

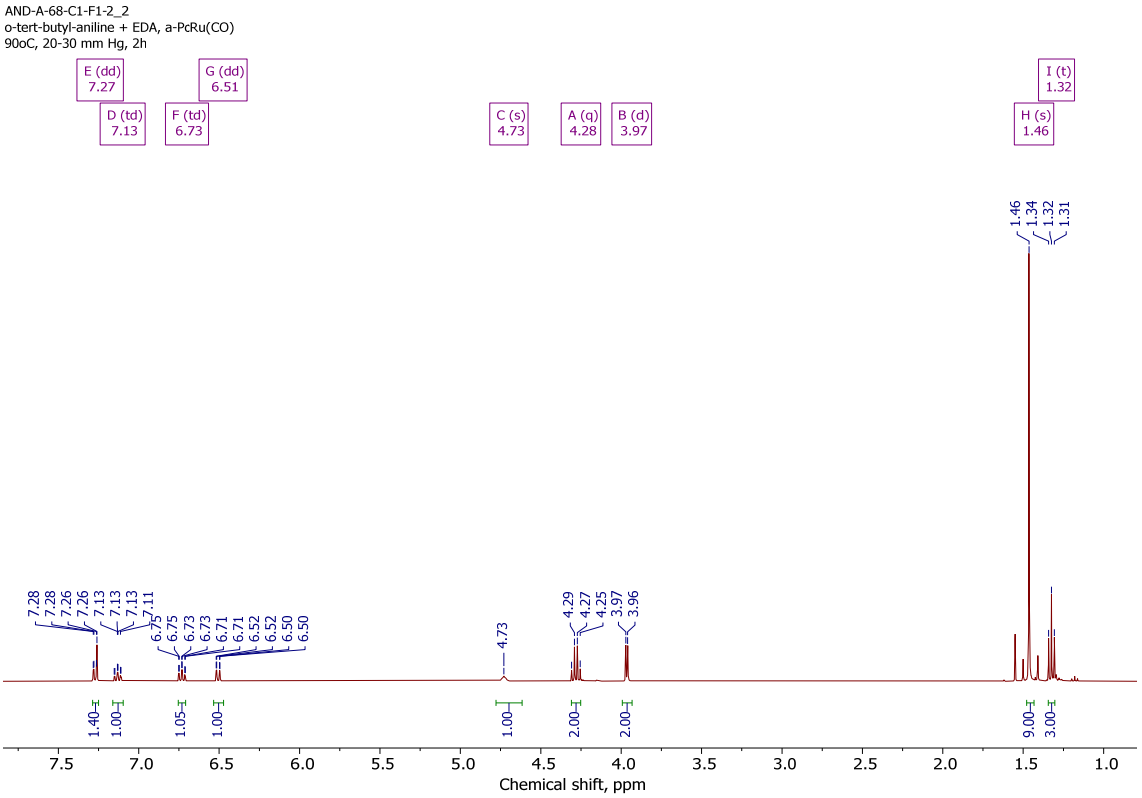


Figure S76. ^{1}H NMR spectrum of ethyl (2-(*tert*-butyl)phenyl)glycinate **3i**.

MS (EI) m/z (%): 235 (23.7), 163 (12.5), 162 (100), 146 (23.8), 132 (21.4), 131 (9.5), 130 (10.9), 117 (11.1), 106 (8.9), 91 (11.5).

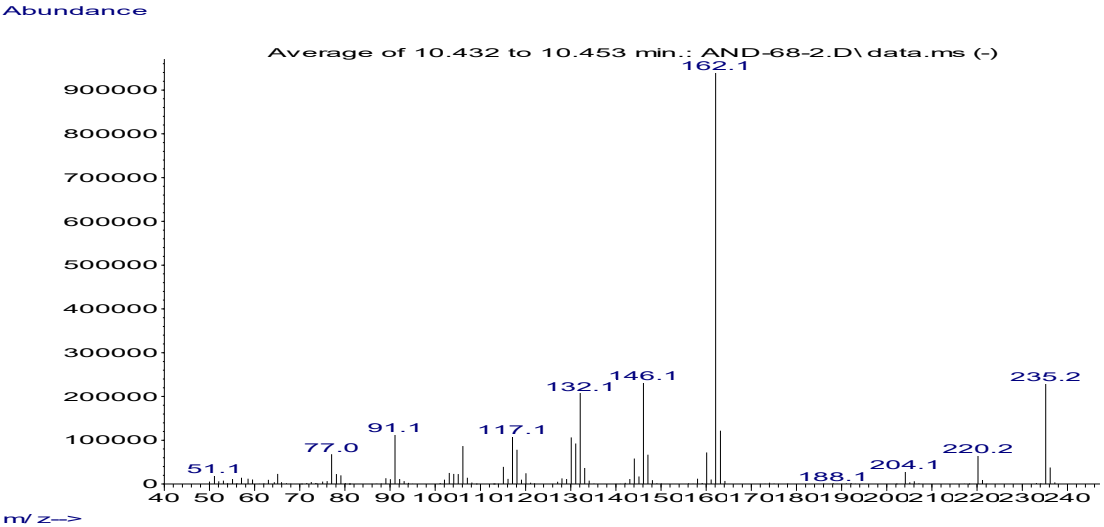


Figure S77. Mass spectrum (EI) of ethyl (2-(*tert*-butyl)phenyl)glycinate **3i**.

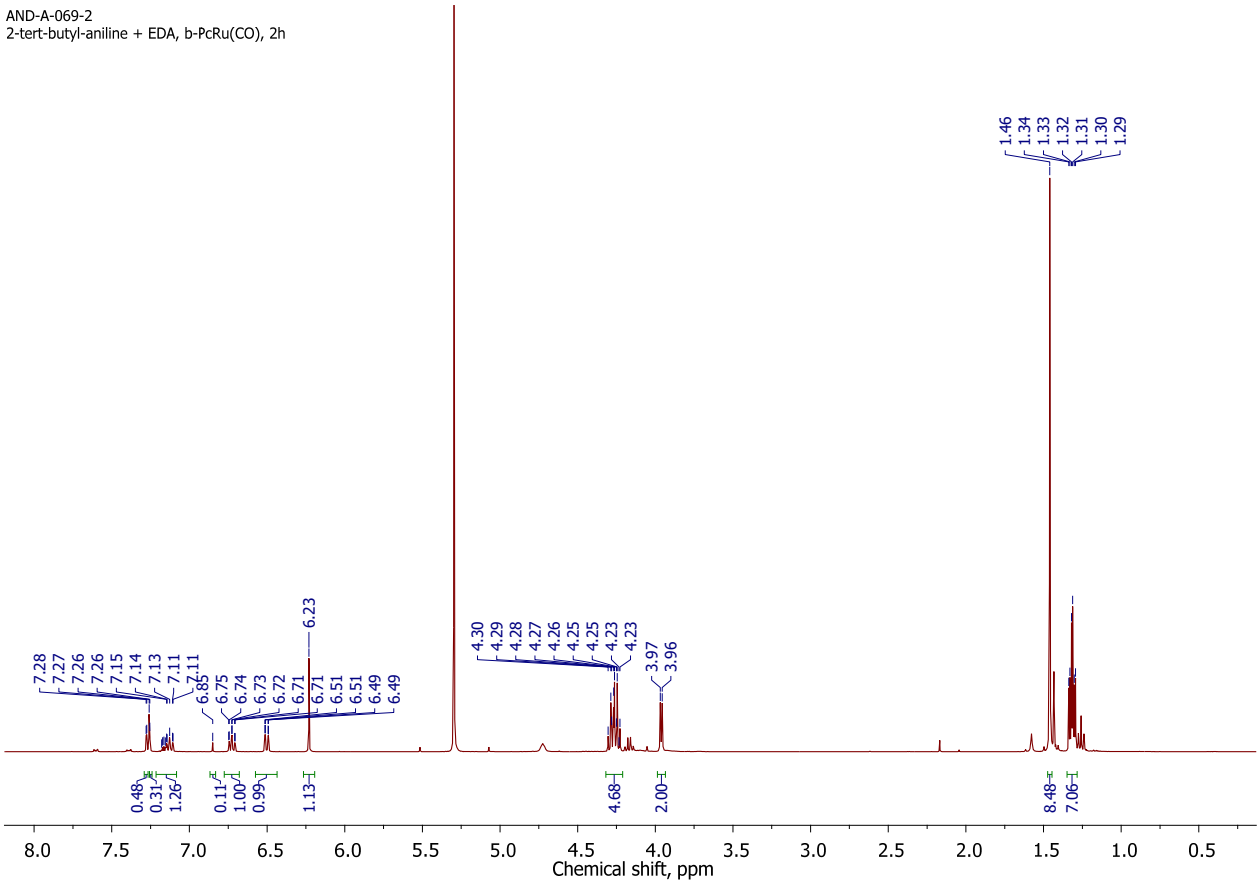


Figure S78. ^{1}H NMR spectrum of the reaction mixture after reaction of EDA with 2-(*tert*-butyl)aniline **2i** in the presence of 0.05 mol. % **1β**.

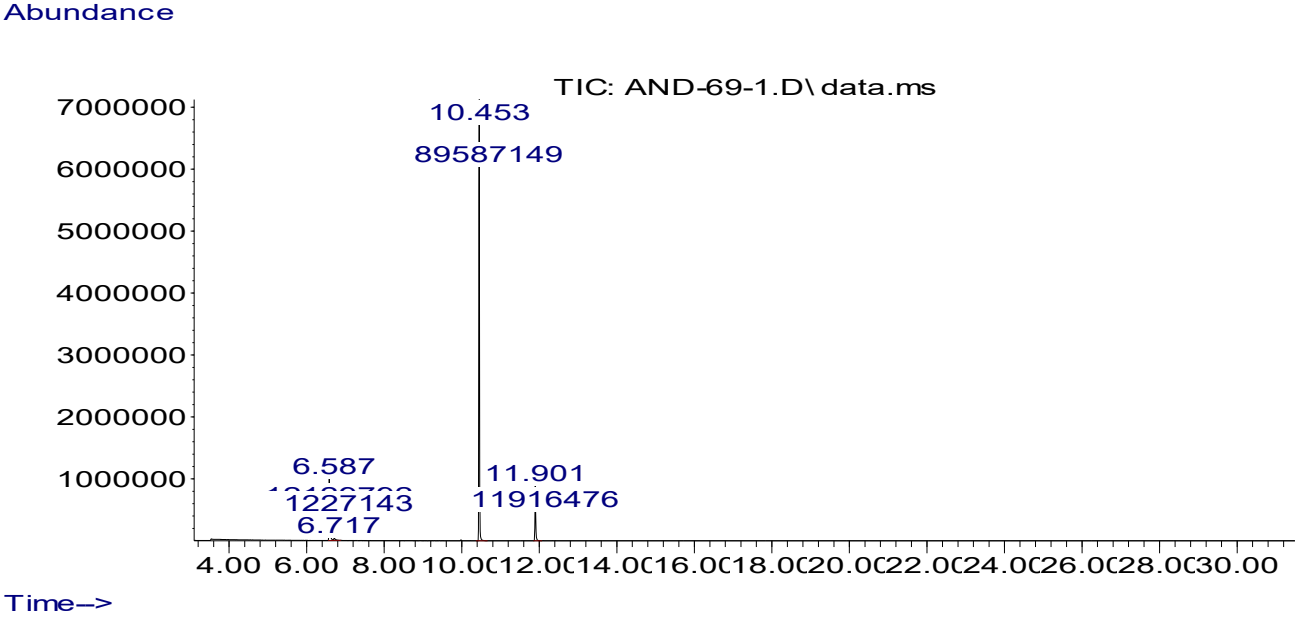


Figure S79. Chromatogram of the reaction mixture after reaction of EDA with 2-(*tert*-butyl)aniline **2i** in the presence of 0.05 mol. % **1β**.

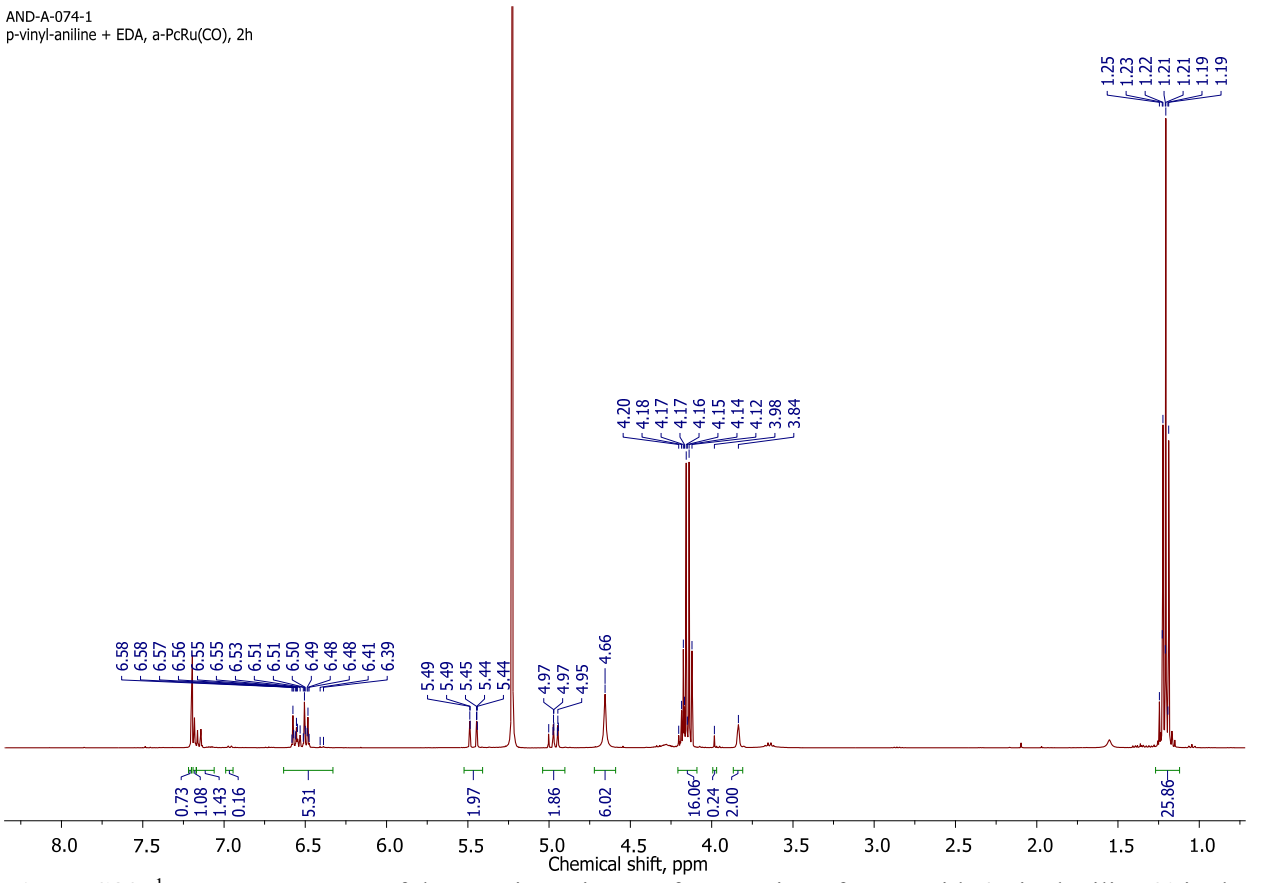


Figure S80. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 4-vinylaniline **2j** in the presence of 0.15 mol. % **1α**.

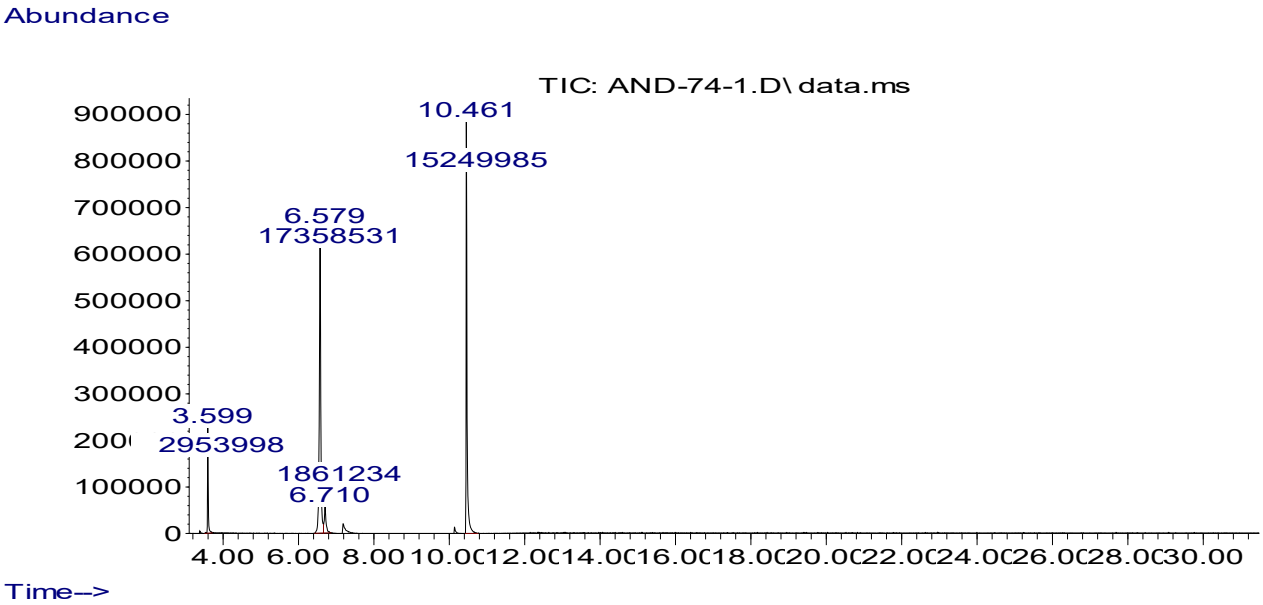
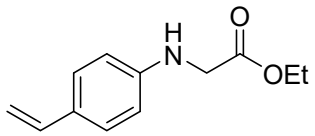


Figure S81. Chromatogram of the reaction mixture after reaction of EDA with 4-vinylaniline **2j** in the presence of 0.15 mol. % **1α**.

Ethyl (4-vinylphenyl)glycinate, 3j



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.27 (dd, J = 6.9, 1.6 Hz, 2H), 6.65 – 6.60 (m, 1H), 6.58 – 6.55 (m, 3H), 5.54 (dd, J = 17.6, 1.0 Hz, 2H), 5.03 (dd, J = 10.9, 1.0 Hz, 1H), 4.34 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.91 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H).

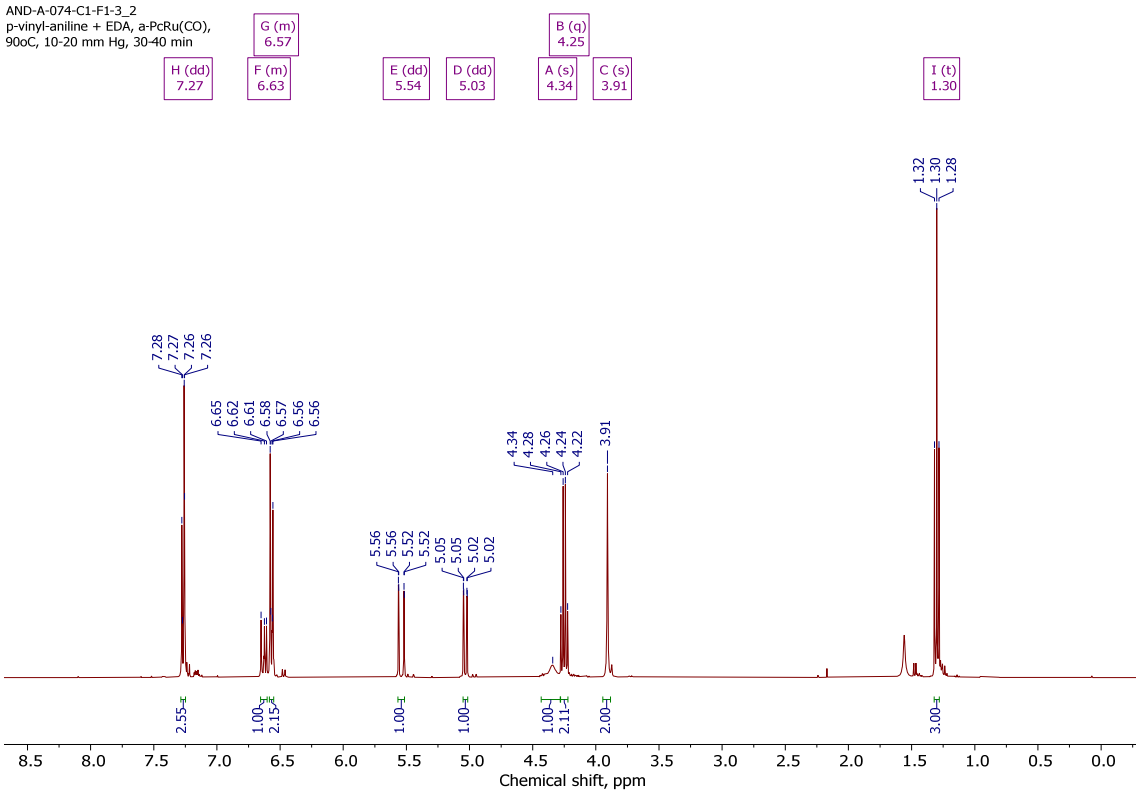


Figure S82. ^{1}H NMR spectrum of ethyl (4-vinylphenyl)glycinate **3j**.

MS (EI) m/z (%): 205 (22.0), 133 (10.1), 132 (100), 131 (4.2), 130 (11.0), 104 (5.2), 103 (10.0), 102 (4.8), 77 (15.1), 51 (3.4).

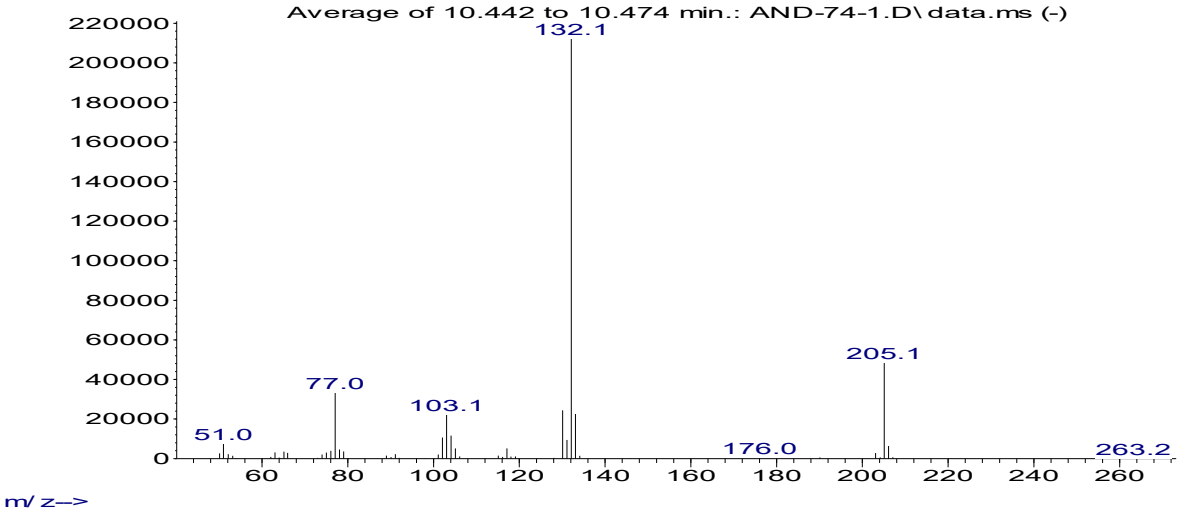


Figure S83. Mass spectrum (EI) of ethyl (4-vinylphenyl)glycinate **3j**.

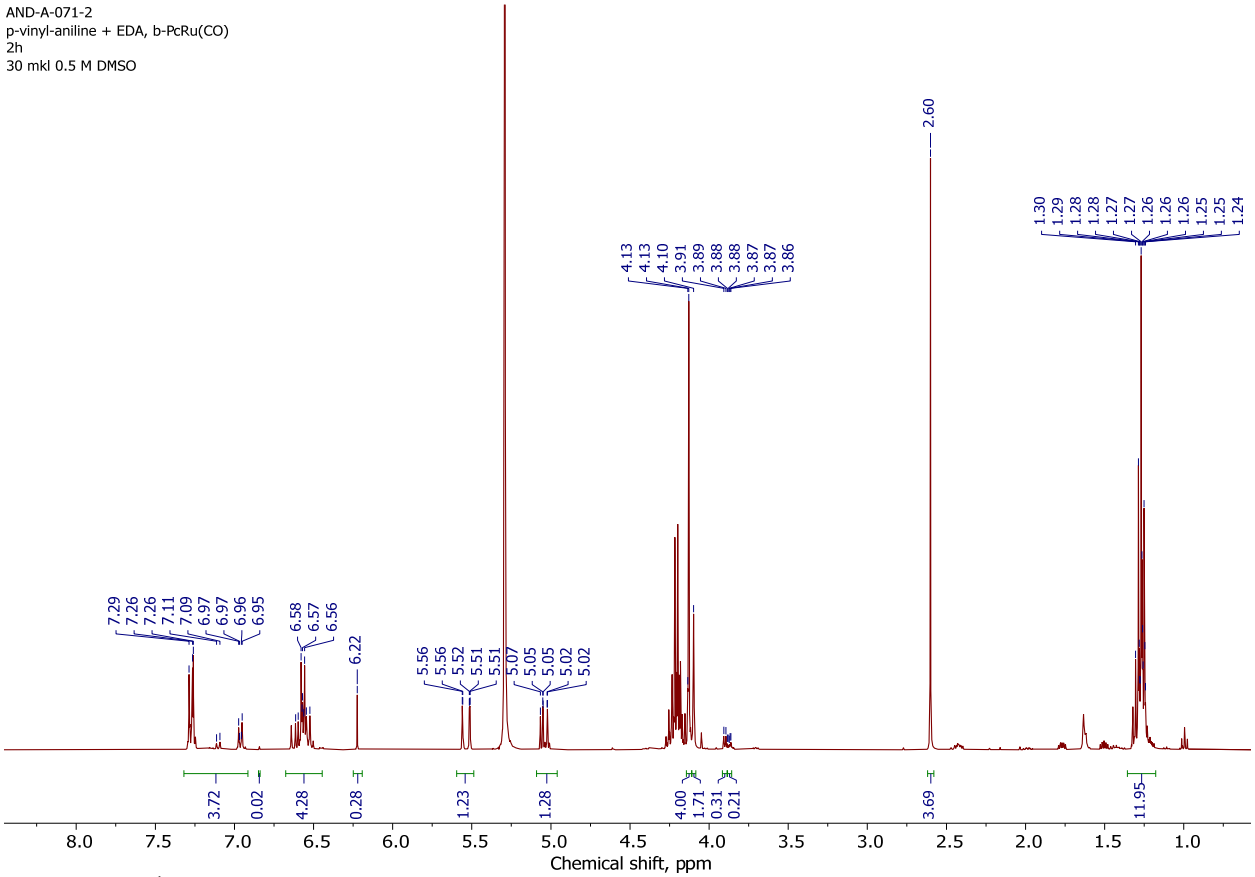


Figure S84. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 4-vinylaniline **2j** in the presence of 0.05 mol. % **1β**.

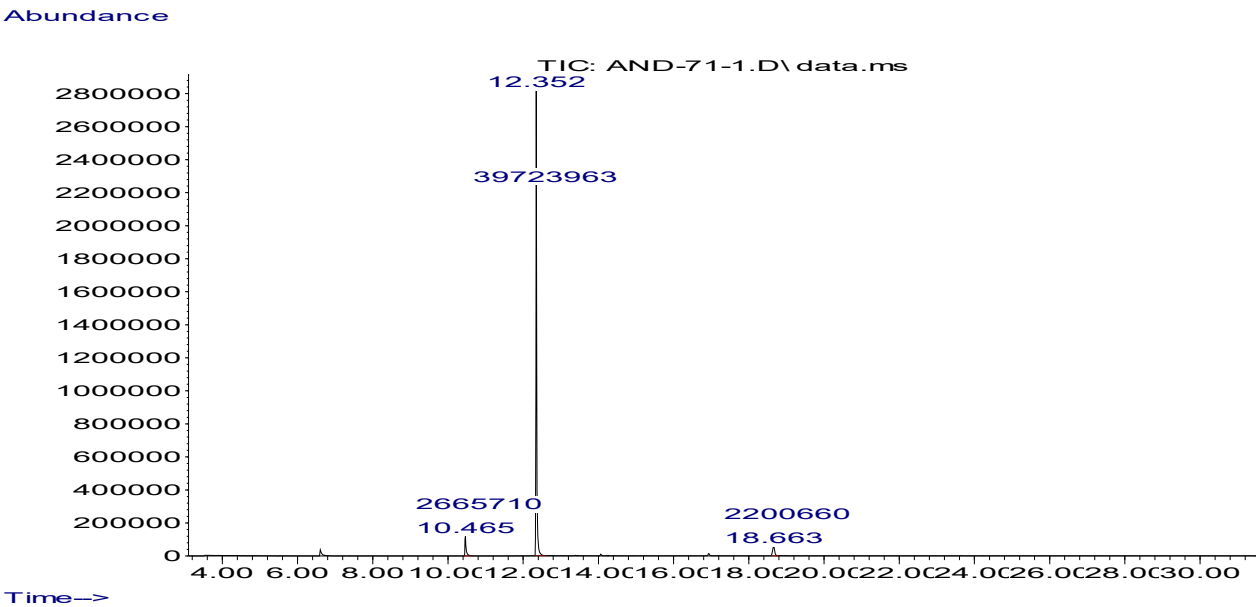
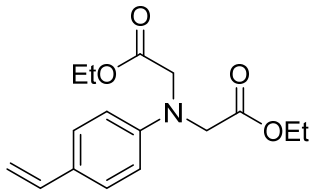


Figure S85. Chromatogram of the reaction mixture after reaction of EDA with 4-vinylaniline **2j** in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((4-vinylphenyl)azanediyl)diacetate, 4j



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.30 – 7.25 (m, 2H), 6.66 – 6.60 (m, 1H), 6.59 – 6.55 (m, 2H), 5.54 (dd, J = 17.6, 1.0 Hz, 1H), 5.04 (dd, J = 10.9, 1.0 Hz, 1H), 4.21 (q, J = 7.1 Hz, 4H), 4.13 (s, 4H), 1.29 – 1.22 (m, 6H).

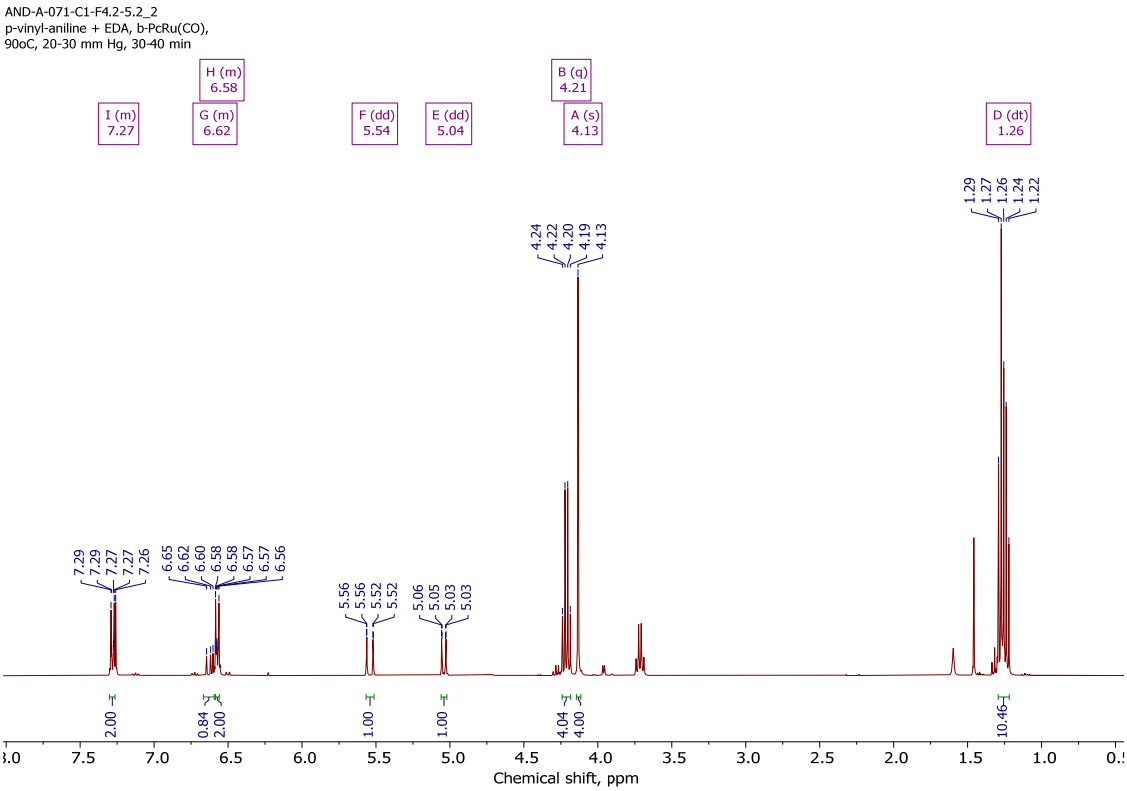


Figure S86. ^{1}H NMR spectrum of diethyl 2,2'-((4-vinylphenyl)azanediyl)diacetate **4j**.

MS (EI) m/z (%): 291 (26.1), 219 (14.7), 218 (100), 146 (19.1), 132 (22.8), 131 (18.9), 130 (20.6), 117 (14.7), 103 (13.0), 59 (21.5).

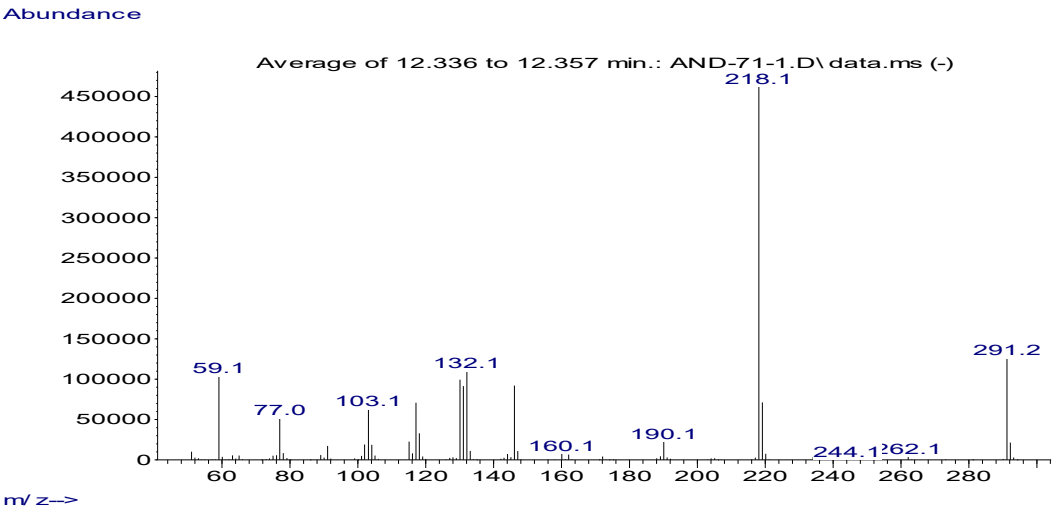
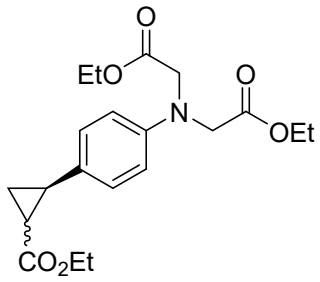


Figure S87. Mass spectrum (EI) of diethyl 2,2'-((4-vinylphenyl)azanediyl)diacetate **4j**.

Diethyl 2,2'-((4-((1S,R;2S,R)-2-(ethoxycarbonyl)cyclopropyl)phenyl)azanediyl)diacetate



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.14 – 7.05 (m, 2H), 6.54 – 6.49 (m, 2H), 4.19 (q, J = 7.1 Hz, 4H), 4.10 (s, 4H), 3.88 (qd, J = 7.1, 2.0 Hz, 2H), 2.46 (dd, J = 16.7, 8.6 Hz, 1H), 1.99 (ddd, J = 9.1, 7.8, 5.6 Hz, 1H), 1.65 – 1.60 (m, 1H), 1.29 – 1.21 (m, 9H).

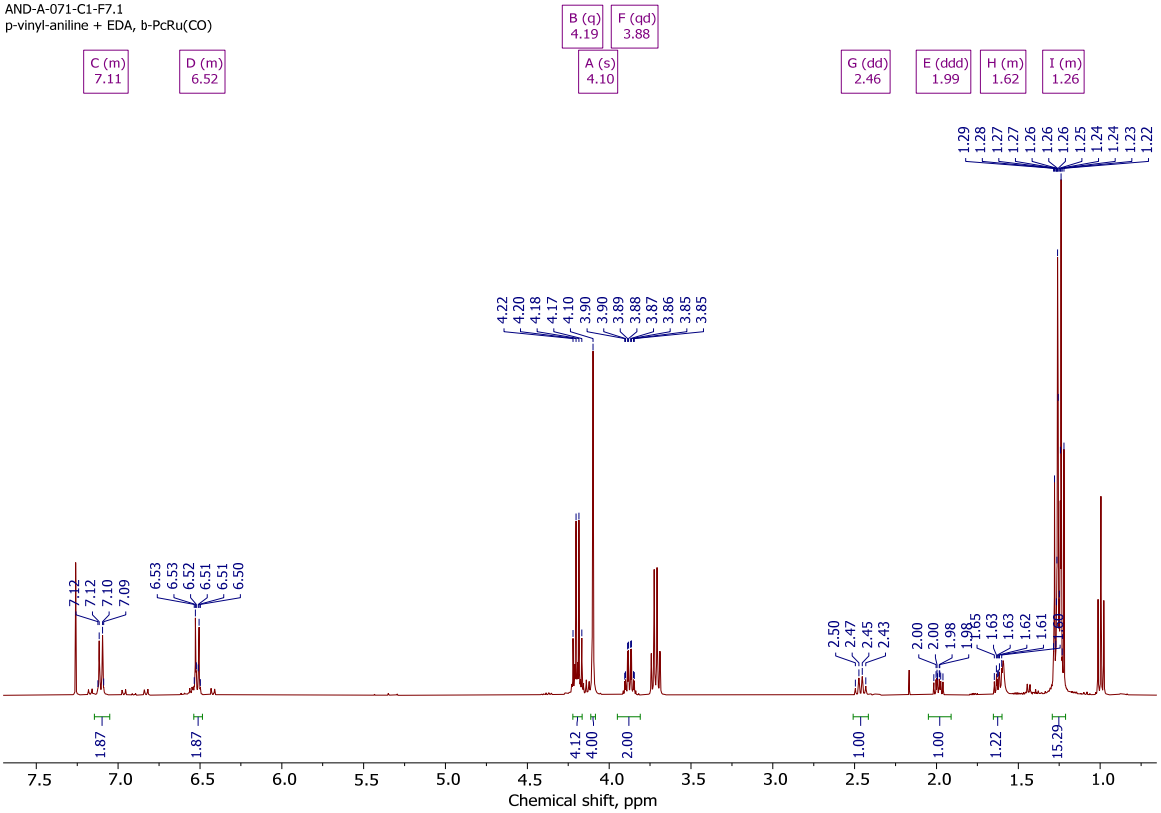


Figure S88. ^{1}H NMR spectrum of diethyl 2,2'-((4-(2-(ethoxycarbonyl)cyclopropyl)phenyl)azanediyl)diacetate, mixture of trans/cis isomers.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 173.68, 171.12, 170.97, 170.85, 146.68, 146.61, 130.06, 129.64, 127.30, 126.11, 112.67, 112.18, 61.11, 61.03, 60.55, 60.10, 53.63, 53.56, 25.65, 24.84, 23.73, 21.85, 16.52, 14.28, 14.23, 14.22, 14.07, 11.15.

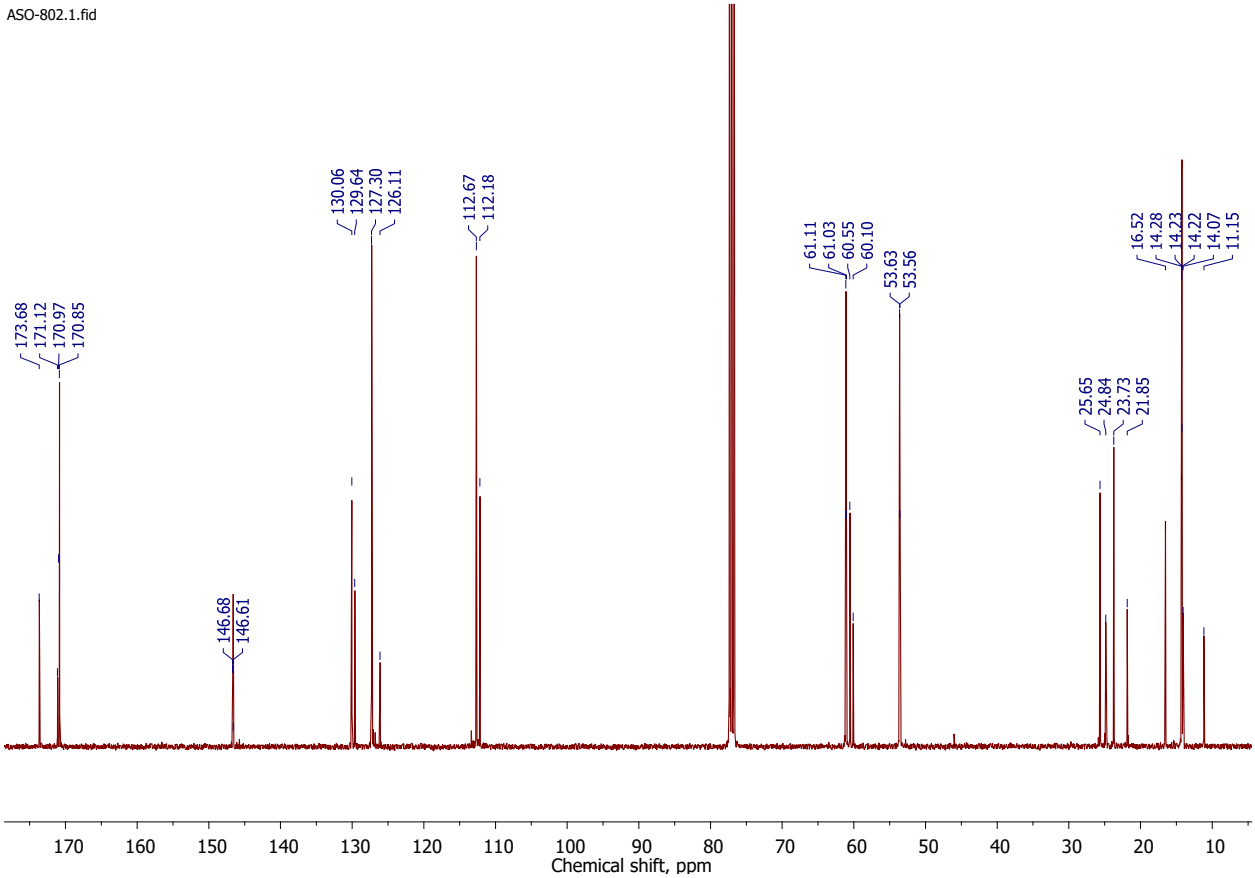


Figure S89. ^{13}C NMR spectrum of diethyl 2,2'-((4-(2-(ethoxycarbonyl)cyclopropyl)phenyl)azanediyl)diacetate, mixture of trans/cis isomers.

MS (EI) m/z (%): 377 (12.6), 305 (19.2), 304 (100), 290 (6.7), 232 (10.0), 144 (28.9), 117 (7.7), 116 (19.1), 115 (20.9), 59 (22.9).

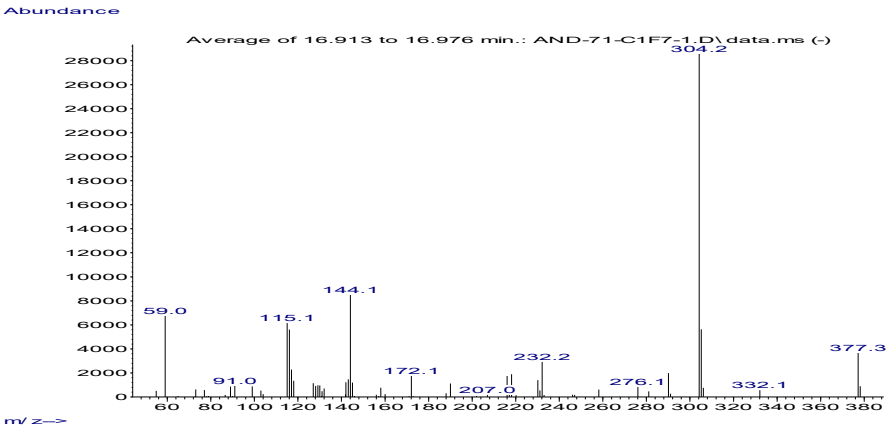


Figure S90. Mass spectrum (EI) of diethyl 2,2'-((4-(2-(ethoxycarbonyl)cyclopropyl)phenyl)azanediyl)diacetate. mixture of trans/cis isomers.

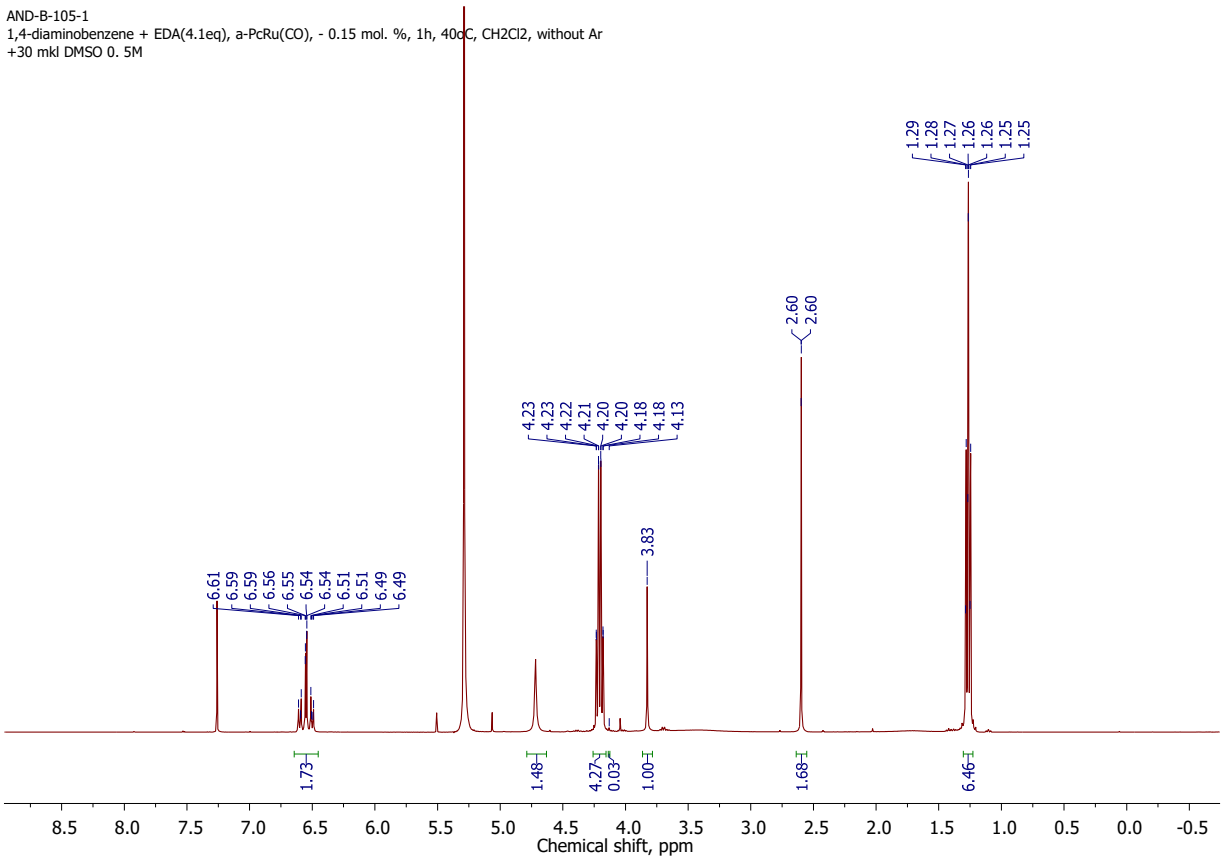


Figure S91. [1]H NMR spectrum of the reaction mixture after reaction of EDA with 1,4-diaminobenzene **5** in the presence of 0.15 mol. % **1α**.

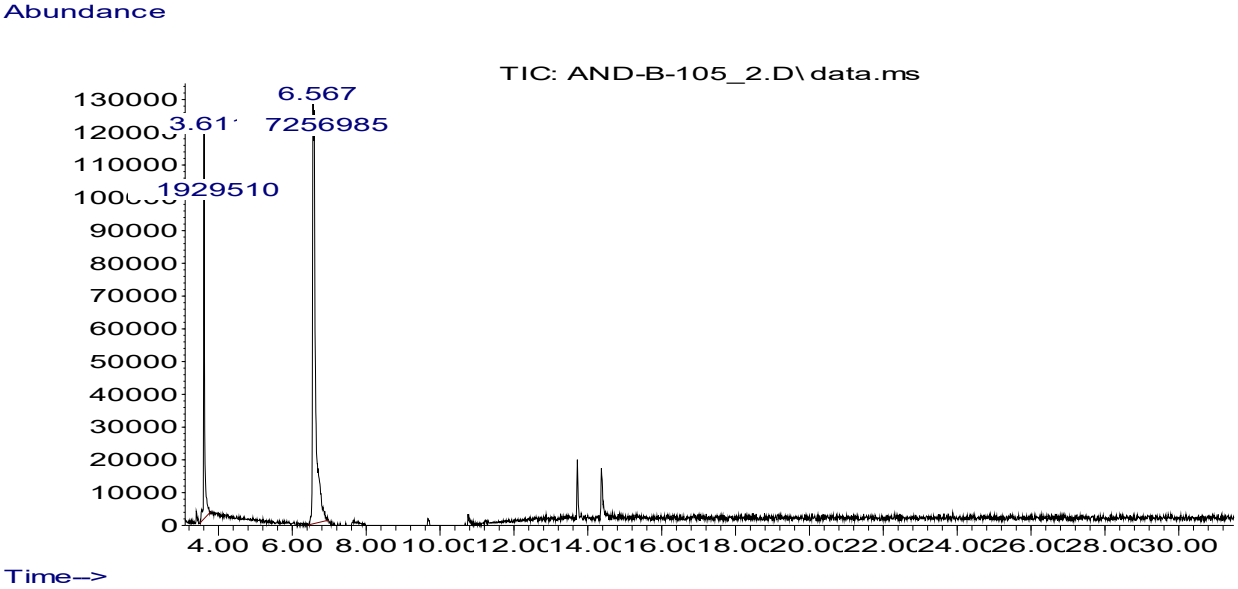
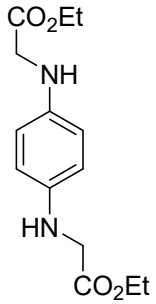


Figure S 92. Chromatogram of the reaction mixture after reaction of 1,4-diaminobenzene **5** with EDA in the presence of 0.15 mol. % **1α**.

Diethyl 2,2'-(1,4-phenylenebis(azanediyl))diacetate 5ss



MS (EI) m/z (%): 281 (11.7), 280 (30.7), 208 (13.6), 207 (100), 179 (21.9), 134 (7.1), 133 (25.9), 106 (8.0), 105 (15.6), 67 (9.1).

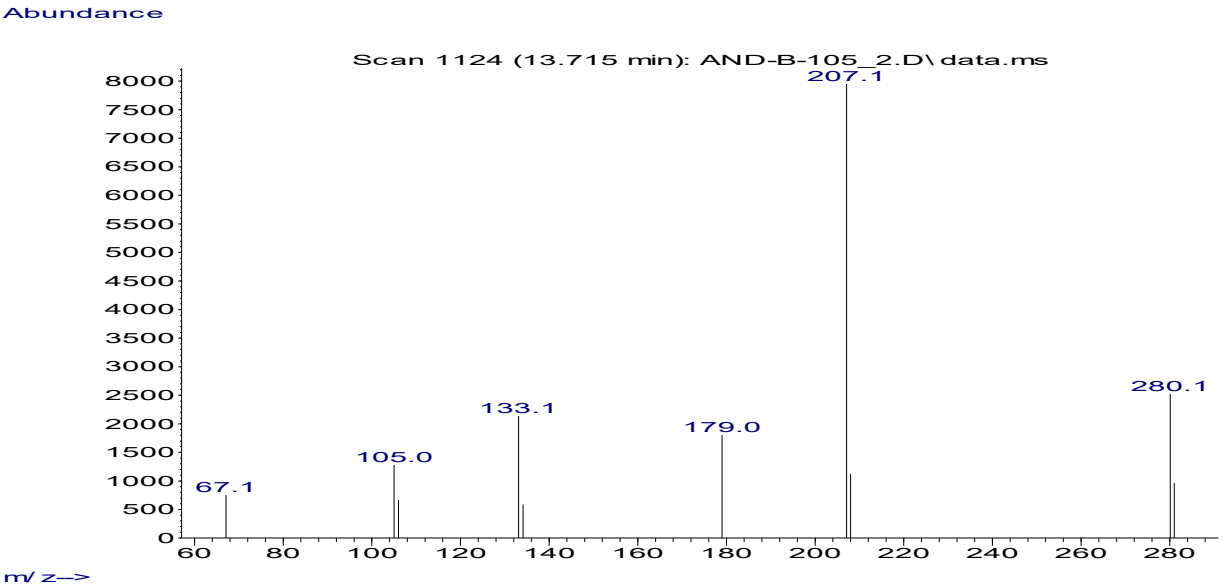


Figure S93. Mass spectrum (EI) of diethyl 2,2'-(1,4-phenylenebis(azanediyl))diacetate **5ss**.

Ethyl 2-((4-((2-ethoxy-2-oxoethyl)amino)phenyl)imino)acetate, **5s's**

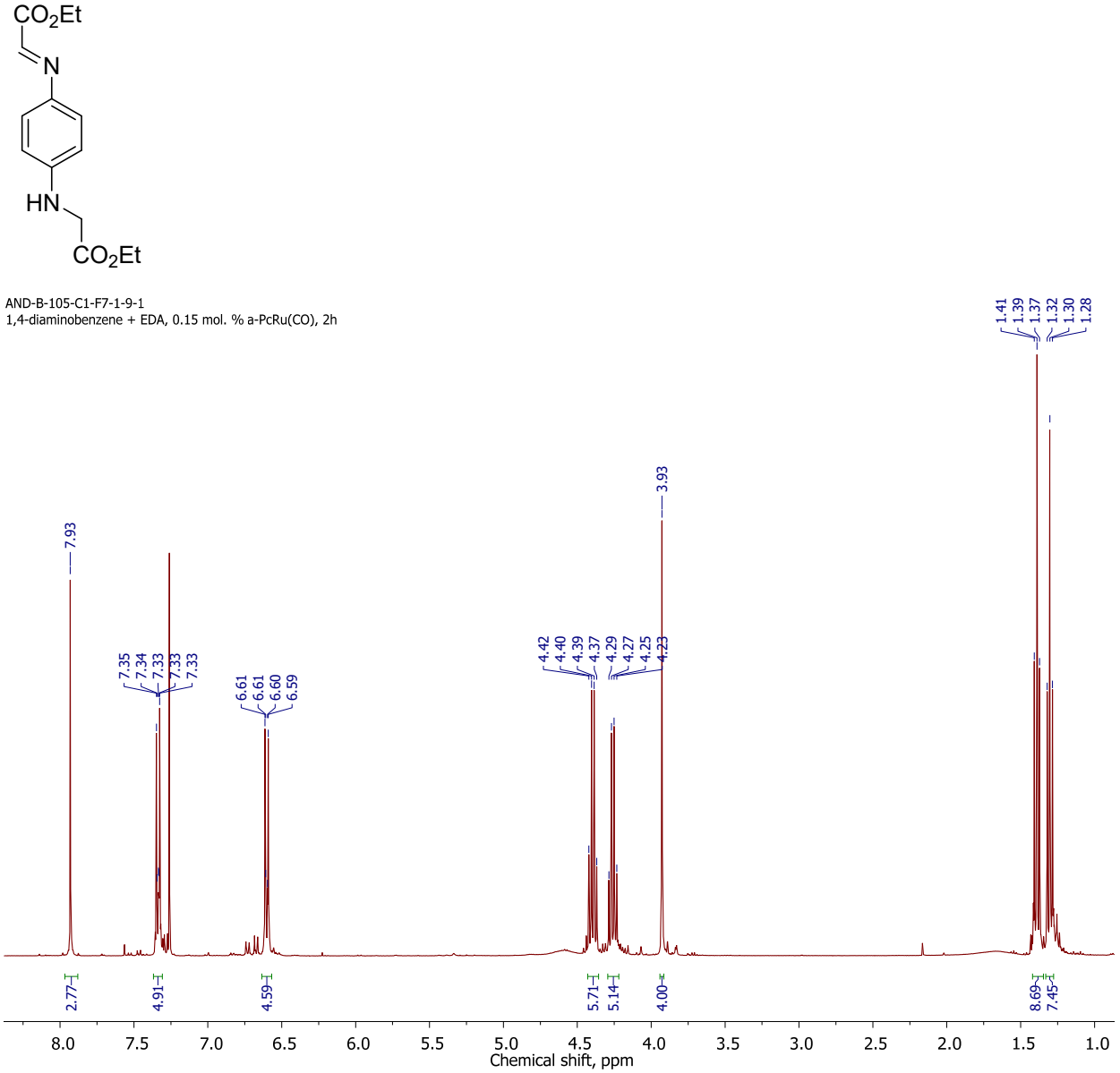


Figure S94. ^{1}H NMR spectrum ethyl 2-((4-((2-ethoxy-2-oxoethyl)amino)phenyl)-imino)acetate **5s's**, isolated by chromatography on SiO_2 column after reaction of 1,4-diaminobenzene **5** with EDA in the presence of 0.15 mol. % **1α**.

MS (EI) m/z (%): 278 (34.3), 207 (30.8), 205 (100), 177 (12.1), 133 (15.6), 131 (15.6), 105 (25.5), 104 (12.9), 77 (11.4), 73 (10.9).

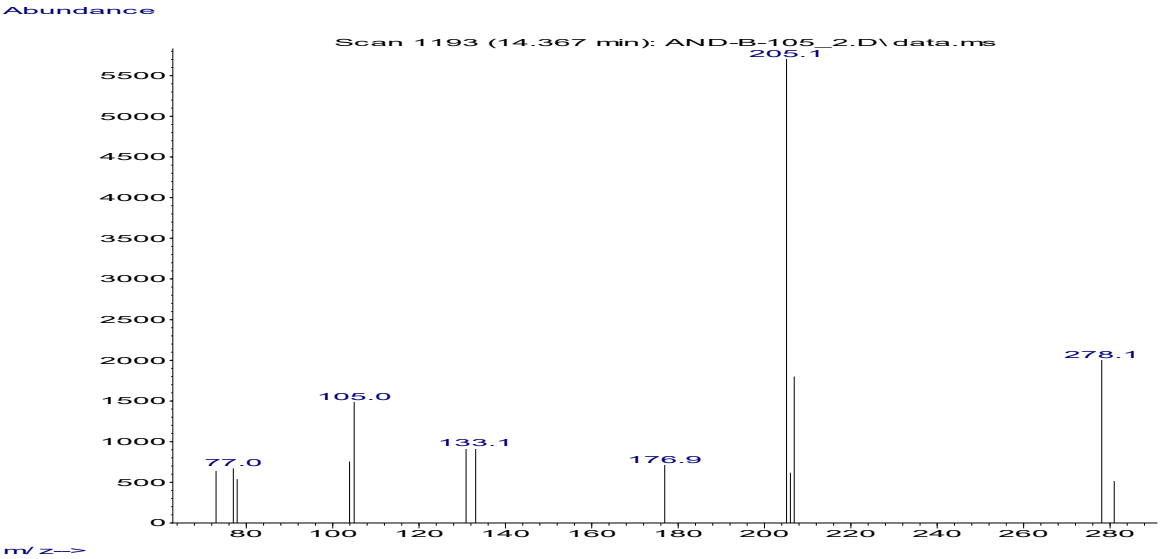


Figure S95. Mass spectrum (EI) of 2-((4-((2-ethoxy-2-oxoethyl)amino)phenyl)imino)acetate **5s's**.

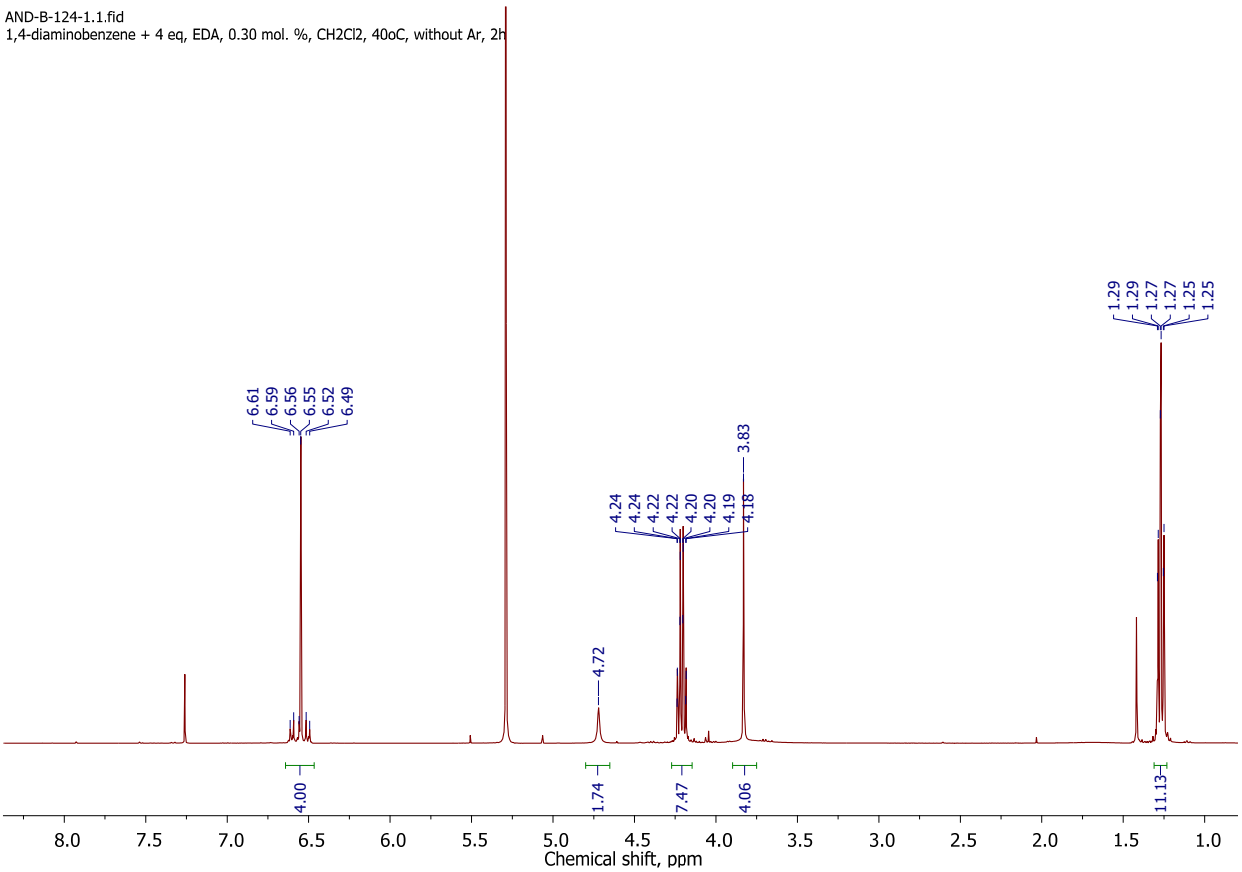


Figure S96. ^{1}H NMR spectrum of the reaction mixture after reaction of 1,4-diaminobenzene **5** with EDA in the presence of 0.30 mol. % **1α**.

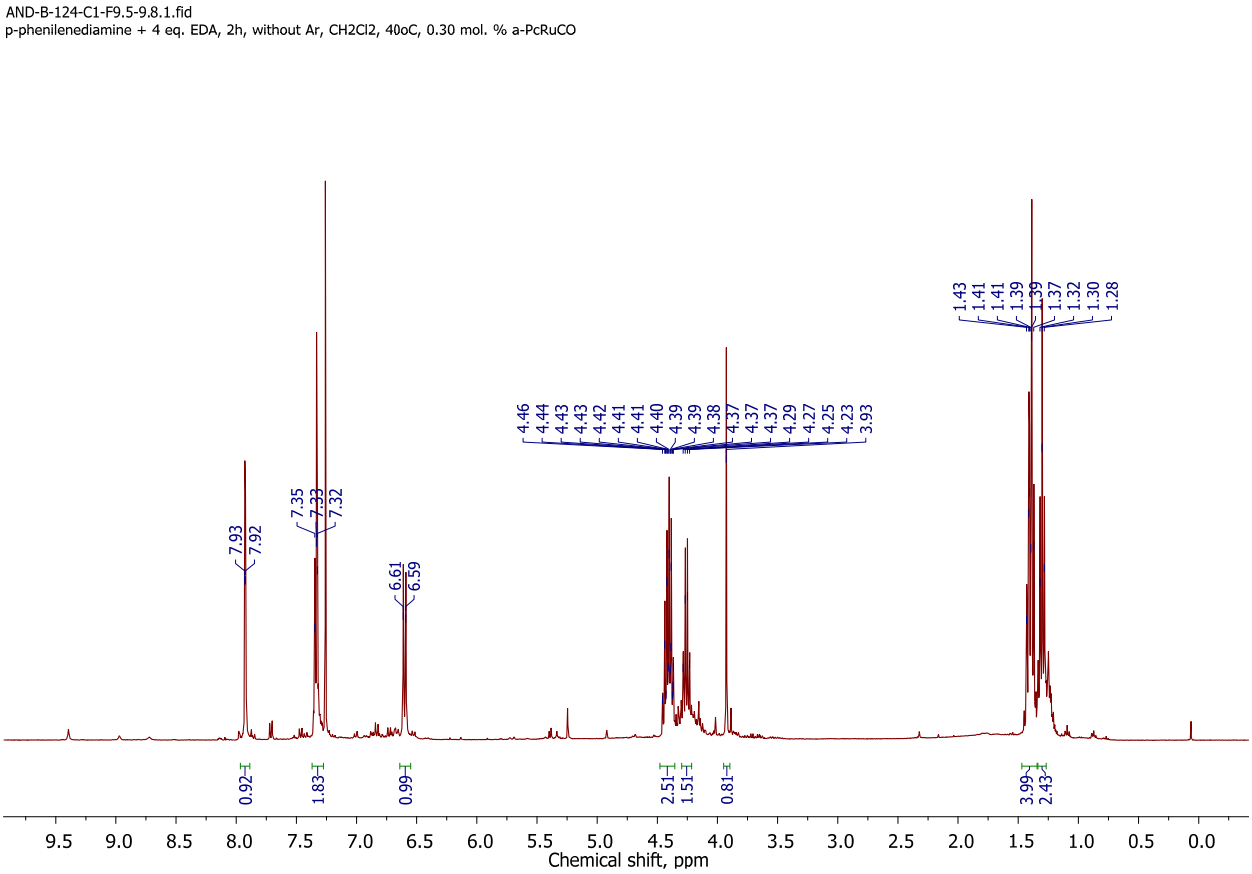


Figure S97. ^{1}H NMR spectrum of mixture of the target SS-insertion product (diethyl 2,2'-(1,4-phenylenebis(azanediyl))diacetate) **5ss** and ethyl 2-((4-((2-ethoxy-2-oxoethyl)amino)phenyl)imino)acetate **5s's**, isolated by chromatography on Al_2O_3 column after reaction of 1,4-diaminobenzene with EDA in the presence of 0.30 mol. % **1α**.

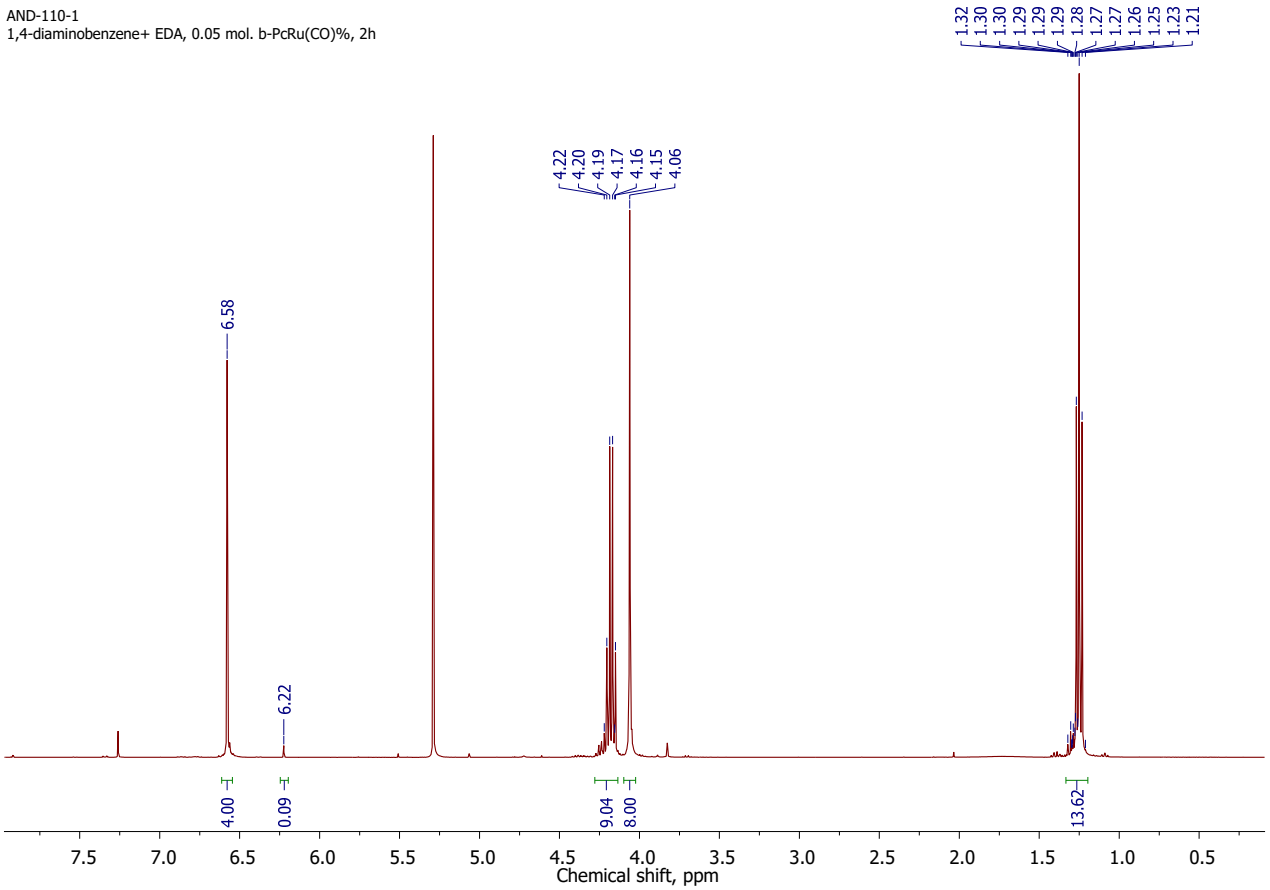


Figure S98. [1]H NMR spectrum of the reaction mixture after reaction of 1,4-diaminobenzene **5** with EDA in the presence of 0.05 mol. % **1β**.

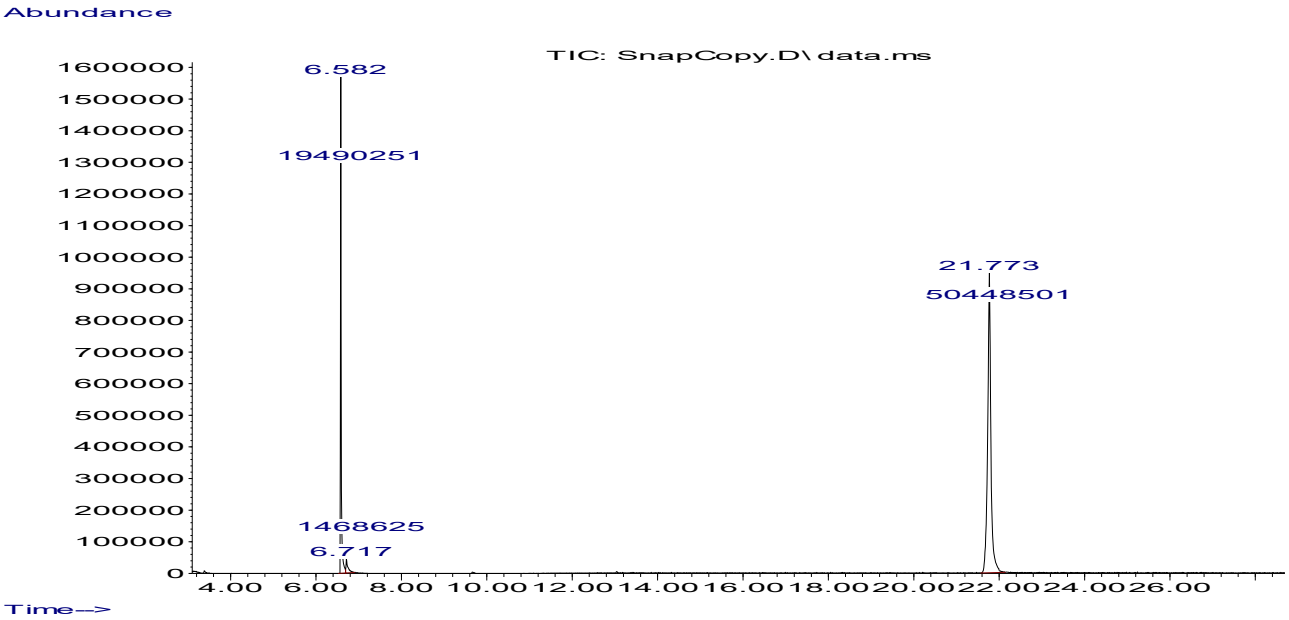
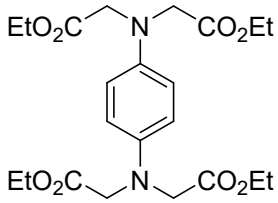


Figure S99. Mass spectrum of the reaction mixture after reaction of 1,4-diaminobenzene **5** with EDA in the presence of 0.05 mol. % **1β**.

Tetraethyl 2,2',2'',2'''-(1,4-phenylenebis(azanetriyl))tetraacetate 5dd



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.58 (s, 4H), 4.18 (q, J = 7.1 Hz, 8H), 4.07 (s, 8H), 1.26 (t, J = 7.1 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 170.31, 123.98, 112.68, 61.38, 53.51, 14.20.

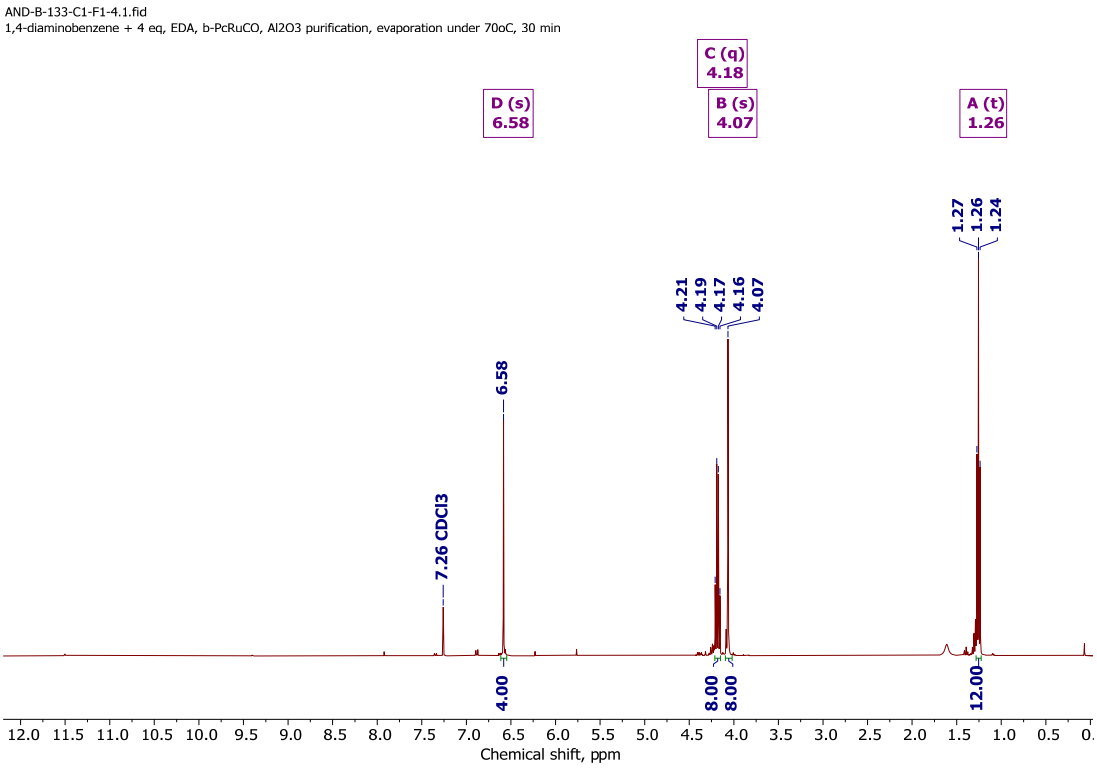


Figure S100. ^{1}H NMR spectrum of tetraethyl 2,2',2",2"'-(1,4-phenylenebis(azanetriyl))tetraacetate **5dd**.

MS (EI) m/z (%): 453 (11.0), 452 (39.5), 380 (21.8), 379 (100), 219 (40.8), 147 (9.6), 133 (12.4), 132 (10.4), 118 (10.1), 59 (16.8).

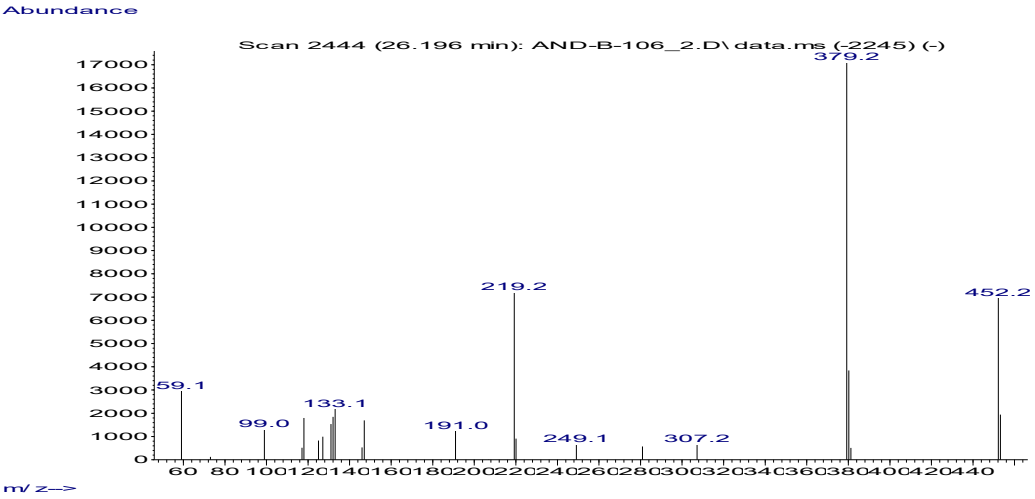


Figure S101. Mass spectrum (EI) of tetraethyl 2,2',2",2"'-(1,4-phenylenebis(azanetriyl))tetraacetate **5dd**.

Diethyl 2,2'-((4-((2-ethoxy-2-oxoethylidene)amino)phenyl)azanediyl)-diacetate, 5s'd

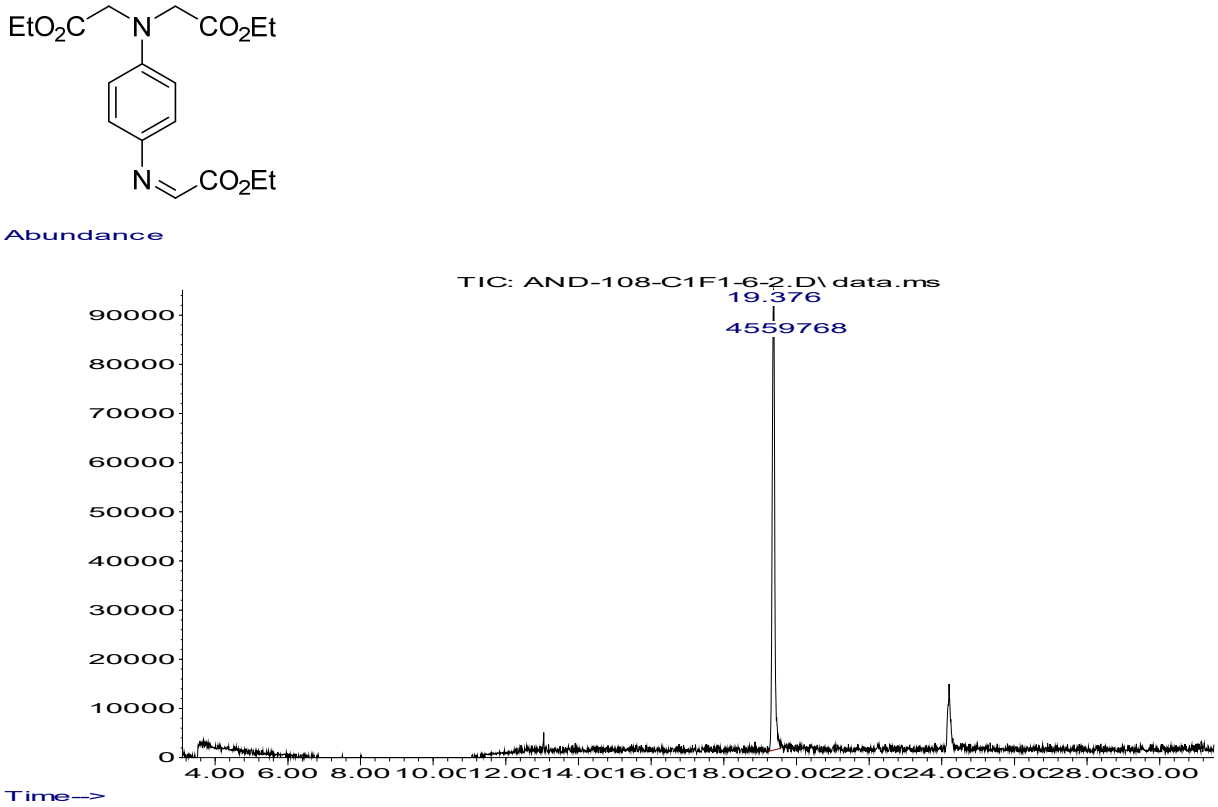


Figure S102. Chromatogram of mixture after chromatographic purification on SiO_2 column. Mass spectrum of the major product corresponds to diethyl 2,2'-((4-((2-ethoxy-2-oxoethylidene)amino)phenyl)azanediyl)-diacetate **5s'd**.

MS (EI) m/z (%): 364 (23.6), 292 (17.1), 291 (100), 219 (8.7), 191 (11.5), 131 (33.8), 105 (6.7), 104 (8.4), 77 (7.5), 59 (23.4).

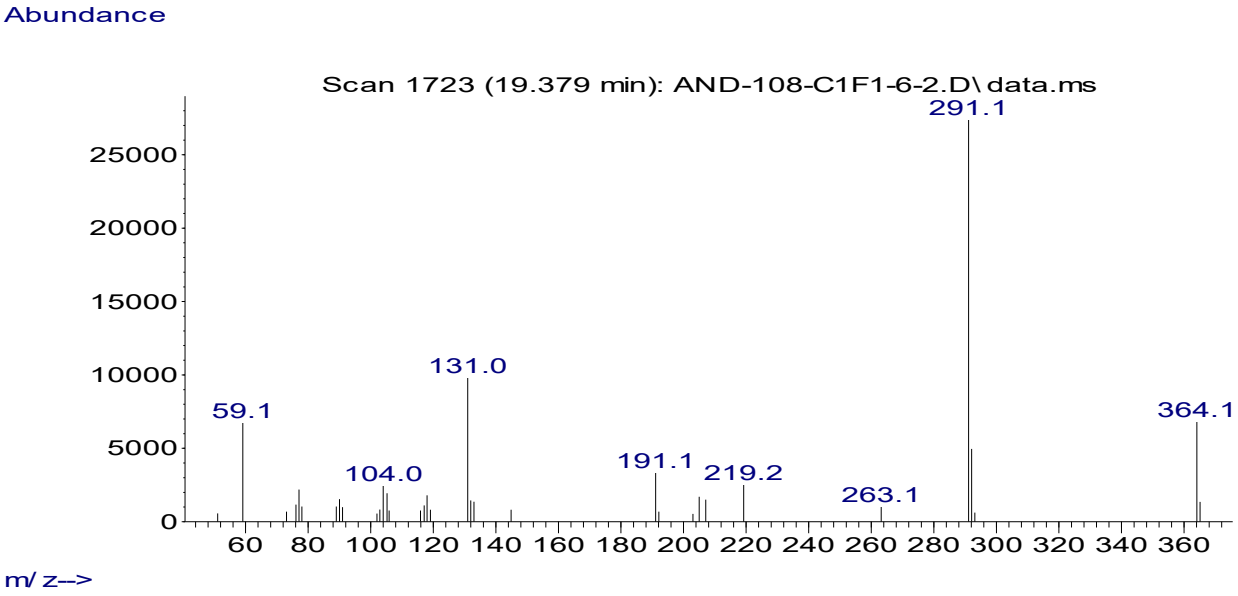


Figure S103. Mass spectrum (EI) of diethyl 2,2'-((4-((2-ethoxy-2-oxoethylidene)amino)phenyl)-azanediyl)-diacetate **5s'd**.

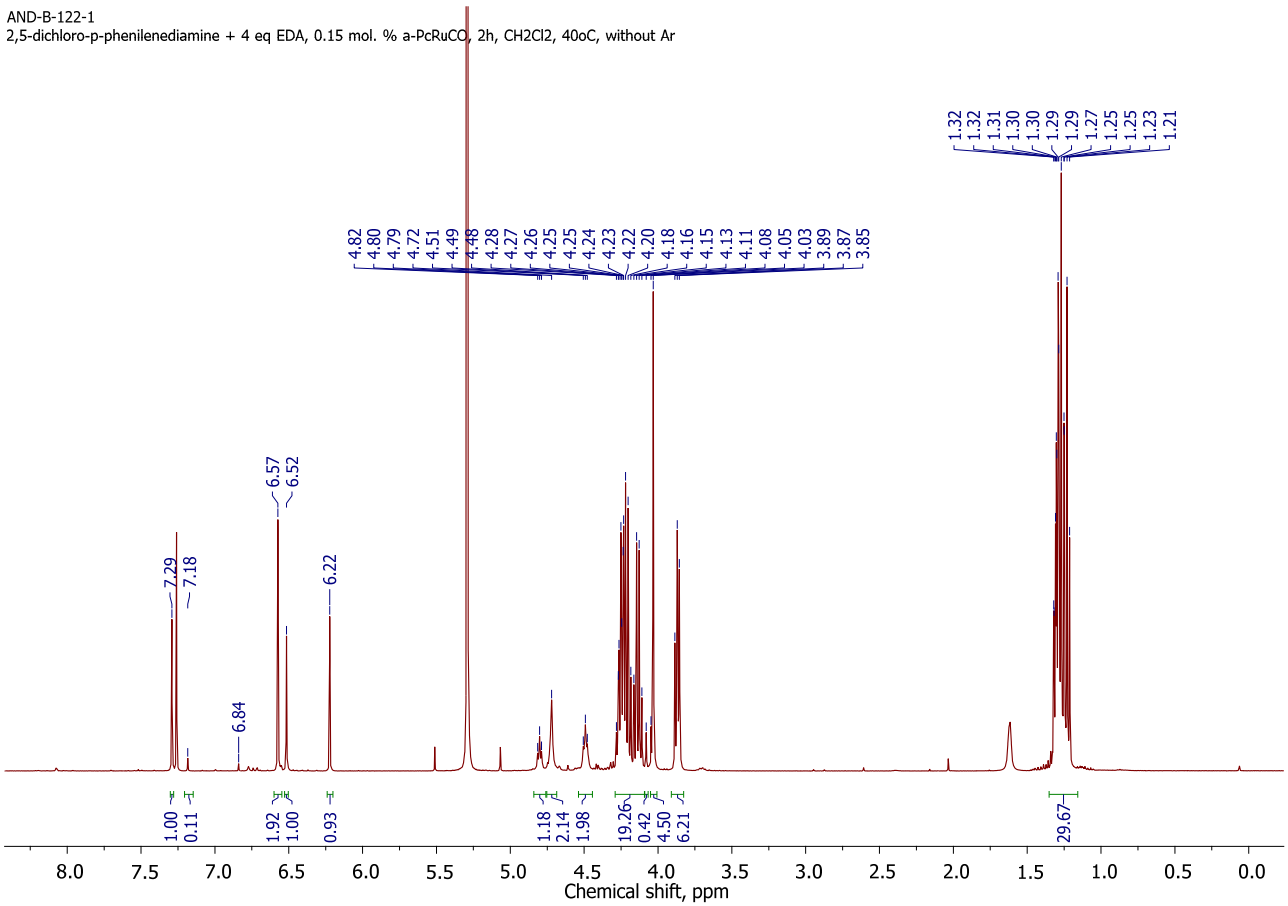


Figure S104. [1]H NMR spectrum of the reaction mixture after reaction of 2,5-dichlorobenzene-1,4-diamine **6** with EDA in the presence of 0.15 mol. % **1α** for 2h.

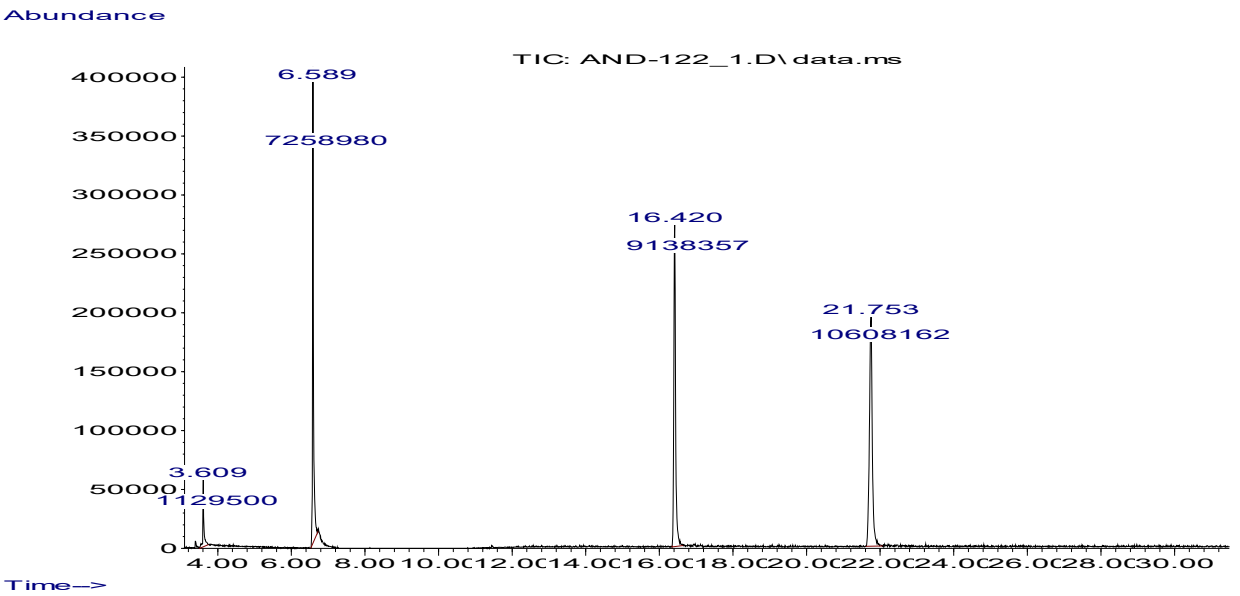
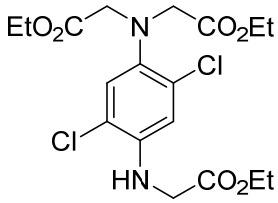


Figure S105. Chromatogram of the reaction mixture after reaction of 2,5-dichlorobenzene-1,4-diamine **6** with EDA in the presence of 0.15 mol. % **1α**. Reaction time: 2 h.

Diethyl 2,2'-((2,5-dichloro-4-((2-ethoxy-2-oxoethyl)amino)phenyl)azanediyl)diacetate, 6sd



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.30 (s, 1H), 6.52 (s, 1H), 4.81 (t, J = 5.3 Hz, 1H), 4.26 (q, J = 7.1 Hz, 3H), 4.14 (q, J = 7.2 Hz, 5H), 4.04 (s, 4H), 3.88 (d, J = 5.3 Hz, 2H), 1.31 (t, J = 7.1 Hz, 4H), 1.24 (t, J = 7.1 Hz, 6H).

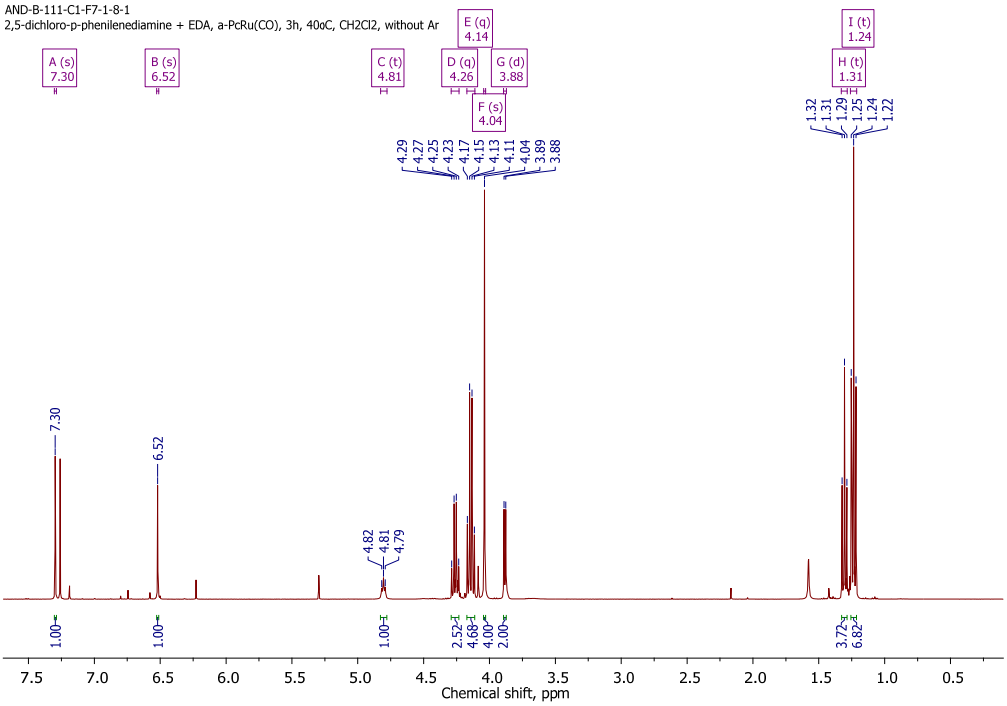


Figure S106. ^{1}H NMR spectrum of diethyl 2,2'-((2,5-dichloro-4-((2-ethoxy-2-oxoethyl)amino)phenyl)azanediyl)diacetate **6sd**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 170.78, 170.15, 140.47, 137.08, 129.61, 126.27, 117.65, 112.20, 61.56, 60.69, 54.43, 45.54, 14.14.

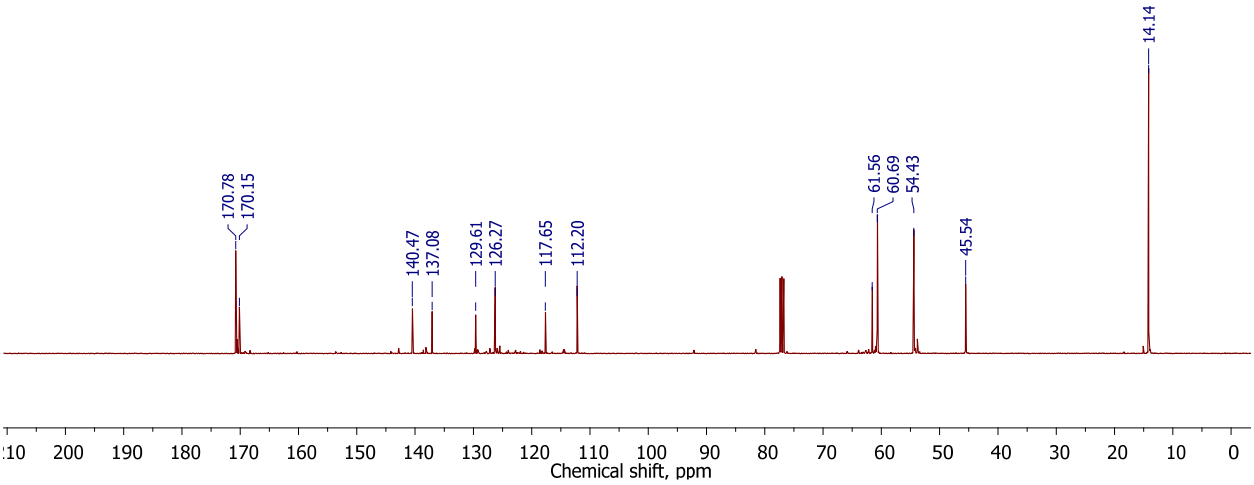


Figure S107. ^{13}C NMR spectrum of diethyl 2,2'-((2,5-dichloro-4-((2-ethoxy-2-oxoethyl)amino)phenyl)azanediyl)diacetate **6sd**.

MS (EI) m/z (%): 436 (15.4), 434 (22.0), 363 (63.1), 362 (17.9), 361 (100), 289 (15.8), 287 (20.8), 203 (42.5), 201 (66.5), 59 (31.2).

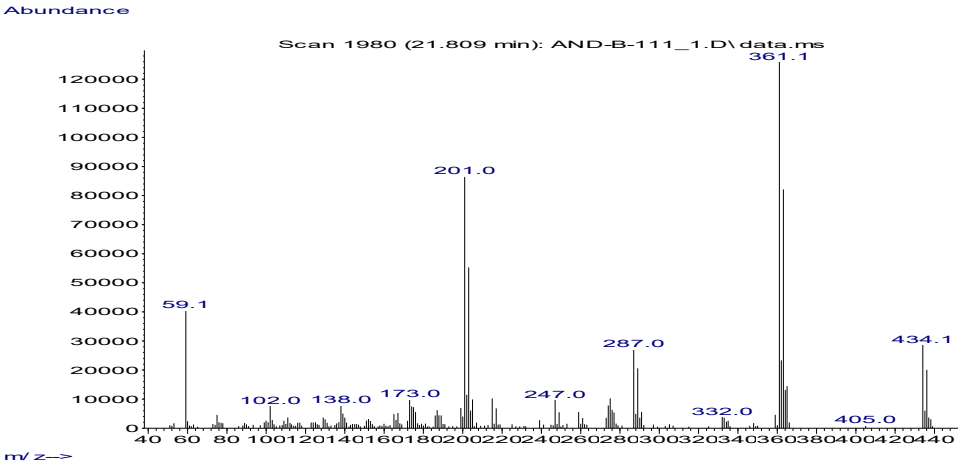


Figure S108. Mass spectrum (EI) of diethyl 2,2'-((2,5-dichloro-4-((2-ethoxy-2-oxoethyl)amino)phenyl)azanediyl)diacetate **6sd**.

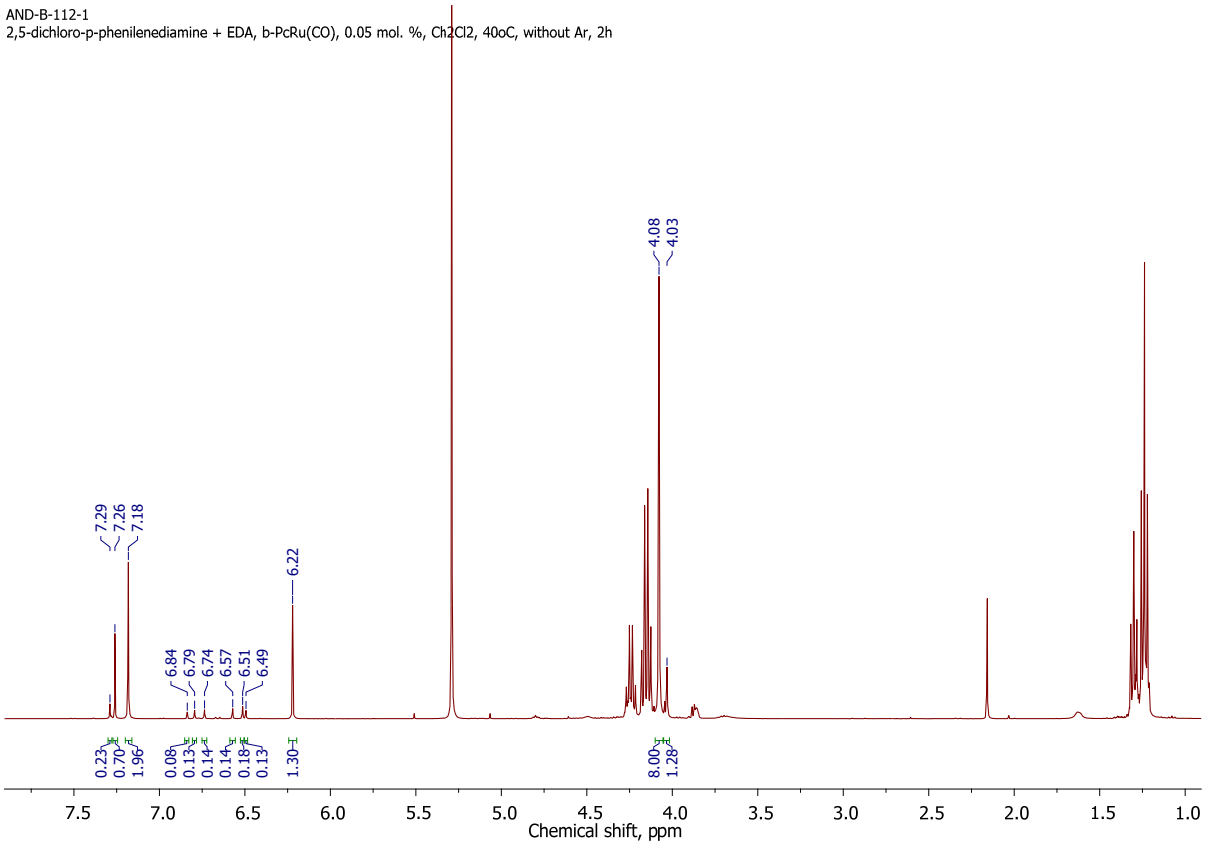
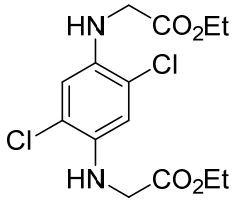


Figure S109. ^{1}H NMR spectrum of the reaction mixture after reaction of 2,5-dichlorobenzene-1,4-diamine **6** with EDA in the presence of 0.05 mol. % **1β**. Reaction time: 3 h.

Diethyl 2,2'-((2,5-dichloro-1,4-phenylene)bis(azanediyl))diacetate, 6ss



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.58 (s, 2H), 4.50 (s, 2H), 4.25 (q, J = 7.1 Hz, 4H), 3.87 (s, 4H), 1.30 (t, J = 7.1 Hz, 6H).

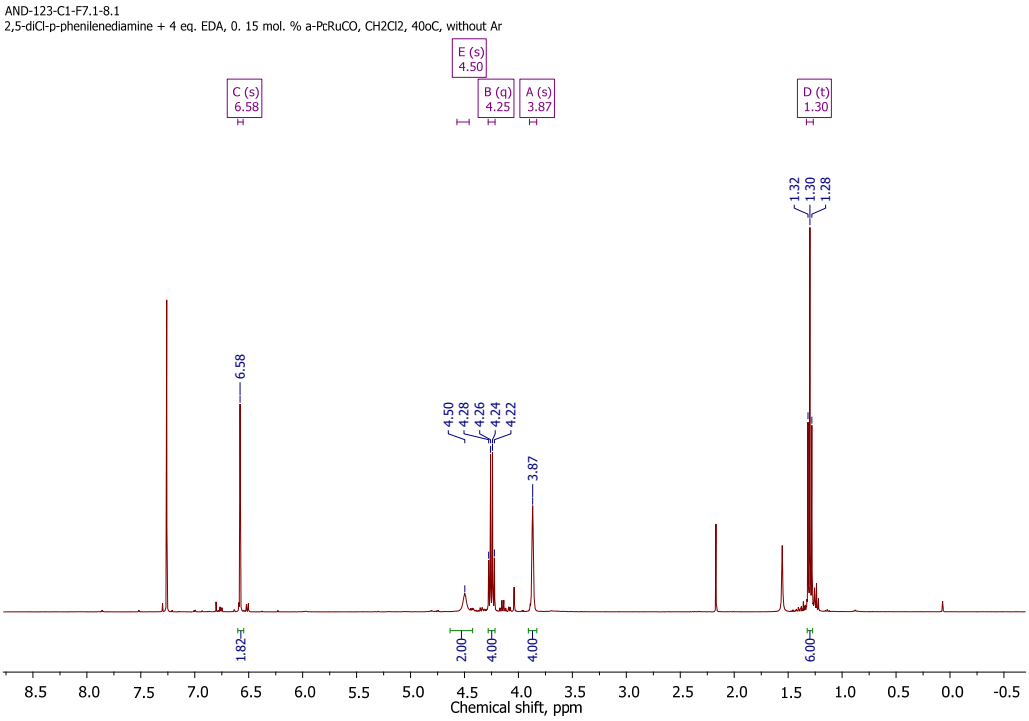


Figure S110. ^{1}H NMR spectrum of diethyl 2,2'-((2,5-dichloro-1,4-phenylene)bis(azanediyl))diacetate, **6ss.**

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 170.58, 135.83, 119.34, 113.36, 61.44, 46.32, 14.17.

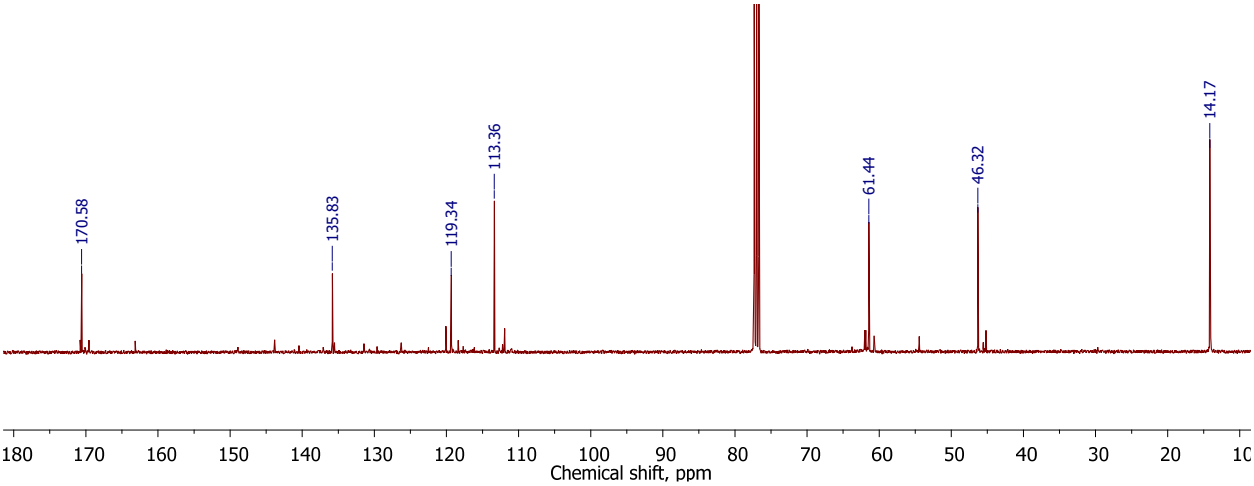


Figure S111. ^{13}C NMR spectrum of diethyl 2,2'-((2,5-dichloro-1,4-phenylene)bis(azanediyl))diacetate **6ss**.

MS (EI) m/z (%): 350 (19.1), 348 (28.4), 277 (63.3), 276 (11.7), 275 (100), 249 (15.2), 247 (23.7), 203 (12.2), 201 (20.0), 173 (15.6).

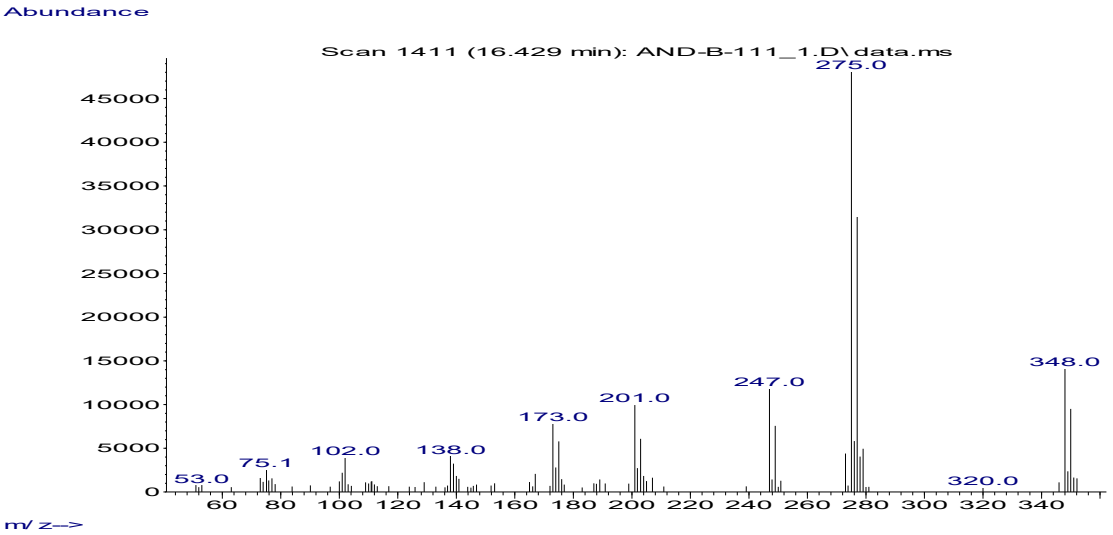
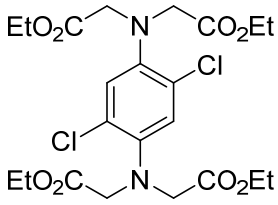


Figure S112. Mass spectrum (EI) of diethyl 2,2'-((2,5-dichloro-1,4-phenylene)bis(azanediyl))diacetate **6ss**.

Tetraethyl 2,2',2'',2'''-((2,5-dichloro-1,4-phenylene)bis(azanetriyl))tetraacetate, 6dd



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.19 (s, 2H), 4.16 (q, J = 7.1 Hz, 8H), 4.08 (s, 8H), 1.25 (t, J = 7.1 Hz, 12H).

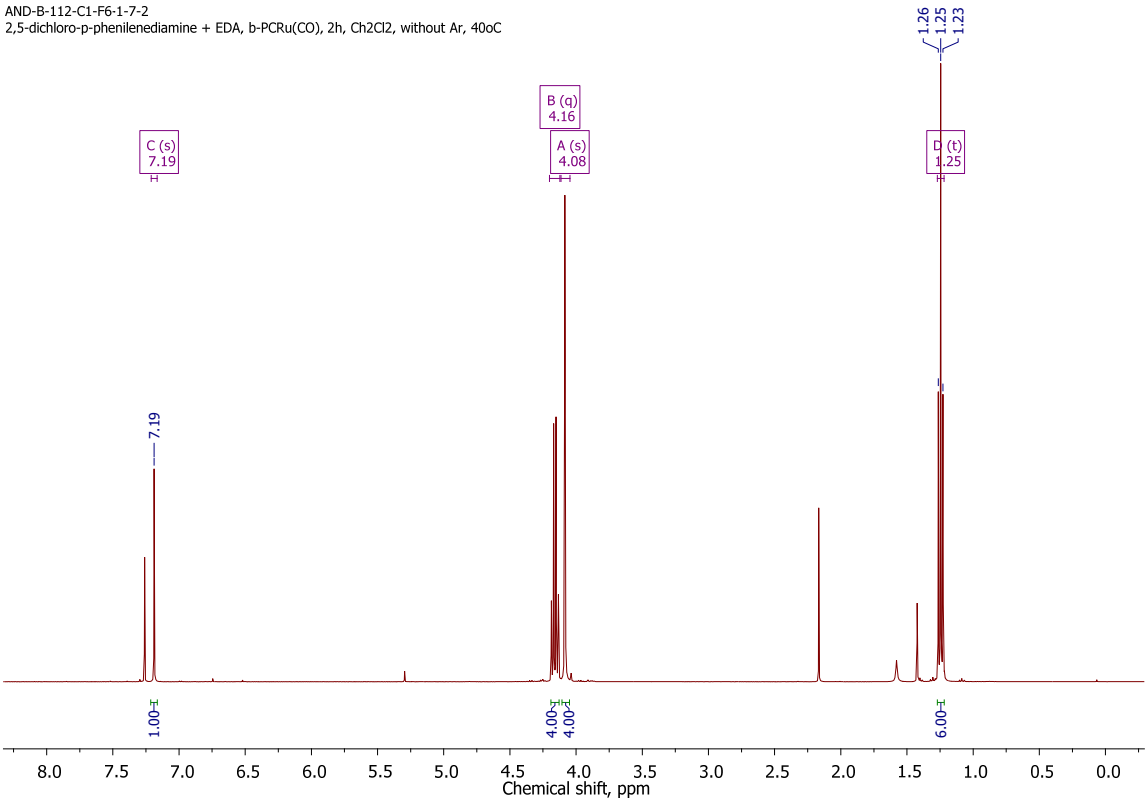


Figure S113. ^{1}H NMR spectrum of tetraethyl 2,2',2'',2'''-((2,5-dichloro-1,4-phenylene)bis(azanetriyl))-tetraacetate **6dd**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 170.46, 142.82, 127.17, 125.46, 60.79, 53.81, 14.12.

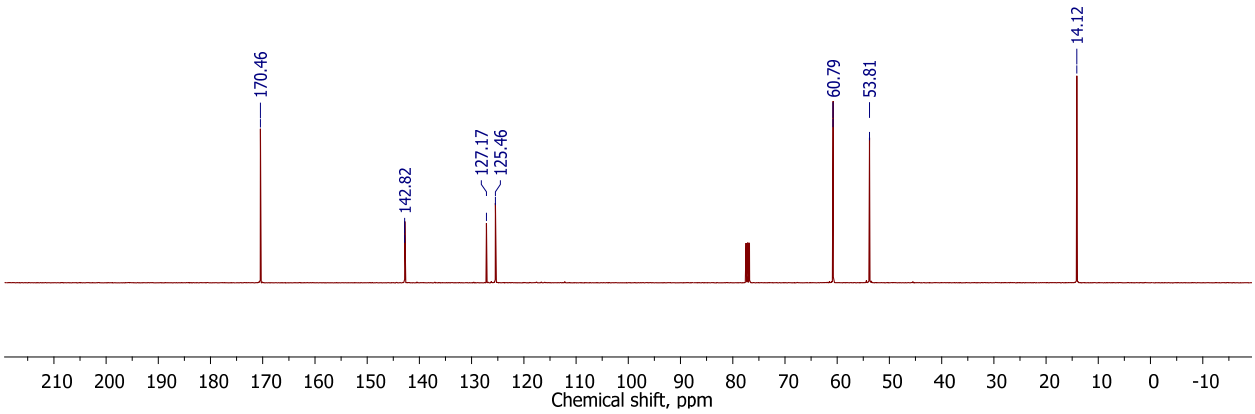


Figure S114. ^{13}C NMR spectrum of tetraethyl 2,2',2",2"'-((2,5-dichloro-1,4-phenylene)bis(azanetriyl))-tetraacetate **6dd**.

MS (EI) m/z (%): 522 (20.6), 520 (22.1), 449 (75.6), 448 (20.4), 447 (100), 287 (26.0), 281 (20.8), 201 (23.6), 73 (22.4), 59 (91.7).

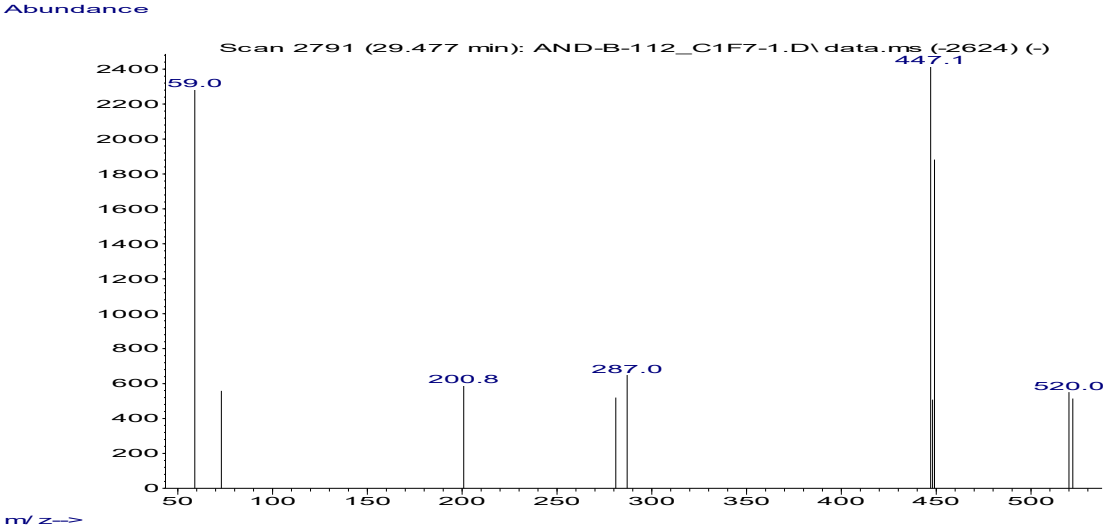


Figure S115. Mass spectrum (EI) of tetraethyl 2,2',2",2"'-((2,5-dichloro-1,4-phenylene)bis(azanetriyl))tetraacetate **6dd**.

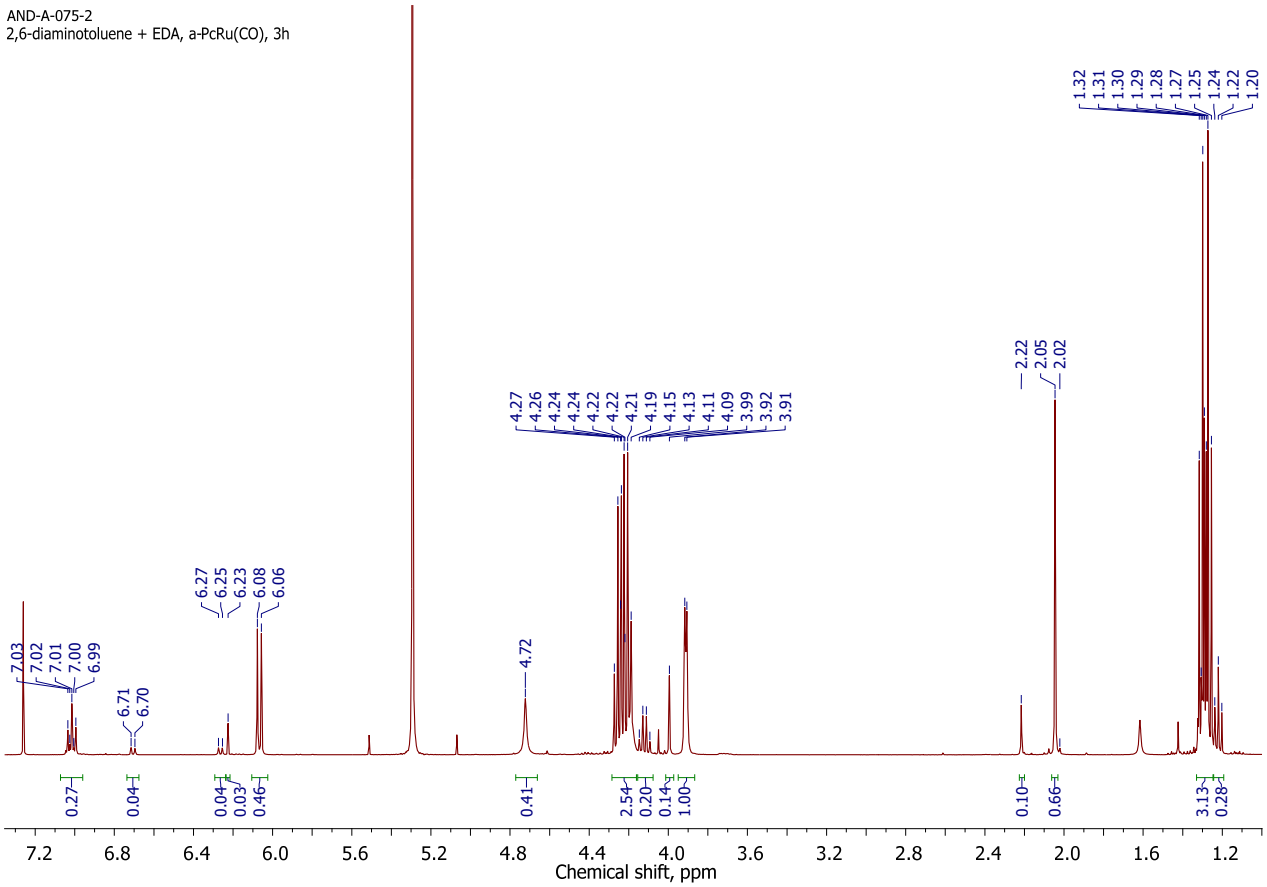


Figure S116. ^{1}H NMR spectrum of the reaction mixture after reaction of 4 equiv. EDA with 2-methylbenzene-1,3-diamine **7** in the presence of 0.15 mol. % **1α**.

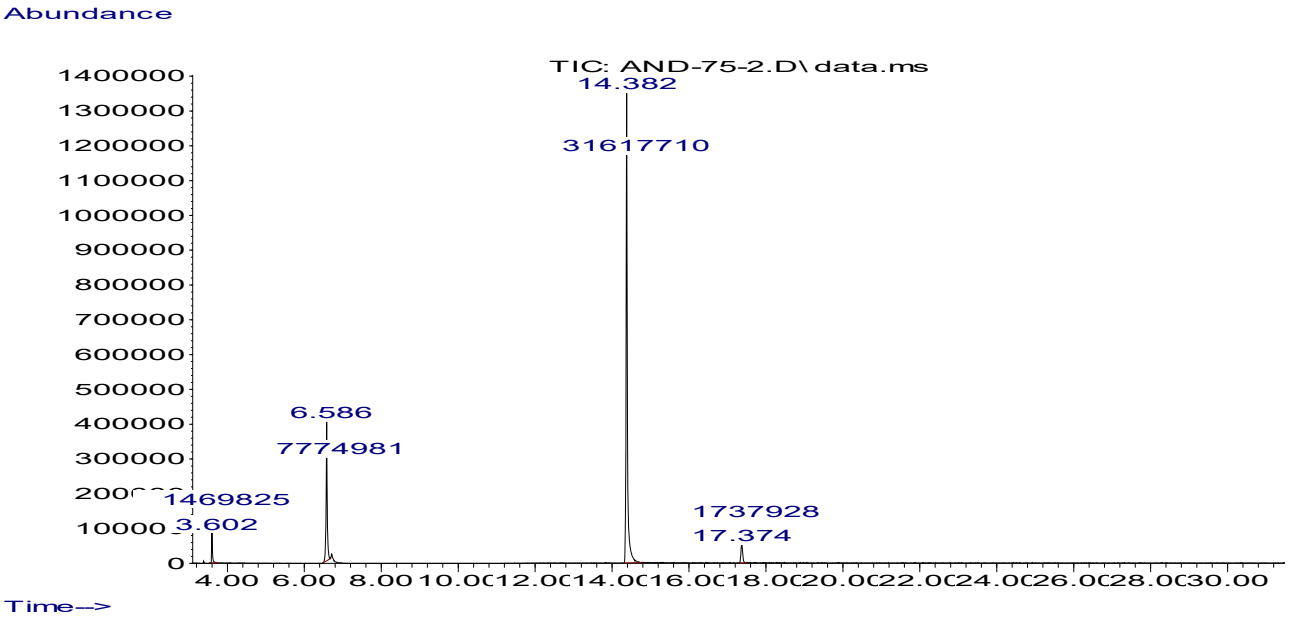
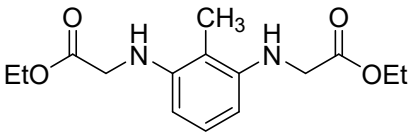


Figure S117. Chromatogram of the reaction mixture after reaction of 2-methylbenzene-1,3-diamine **7** with 4 equiv. EDA in the presence of 0.15 mol. % **1α**.

Diethyl 2,2'-((2-methyl-1,3-phenylene)bis(azanediyl))diacetate **7ss**



^{1}H NMR (400 MHz, CDCl3) (δ, ppm): 7.02 (t, J = 8.1 Hz, 1H), 6.07 (d, J = 8.1 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 4.20 (s, 2H), 3.92 (s, 4H), 2.05 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 171.50, 145.49, 127.17, 106.50, 102.23, 61.25, 46.38, 14.21, 9.69.

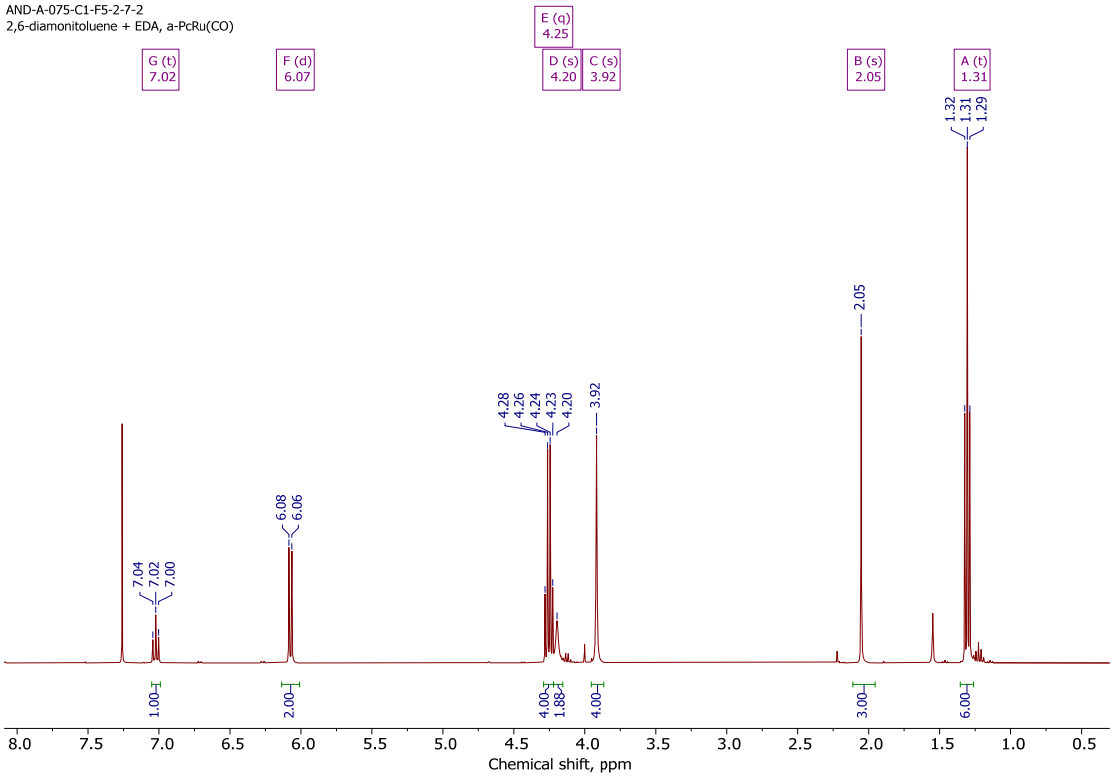


Figure S118. ^{1}H NMR spectrum of diethyl 2,2'-((2-methyl-1,3-phenylene)bis(azanediyl))diacetate **7ss**.

MS (EI) m/z (%): 294 (44.9), 222 (13.7), 221 (100), 219 (14.9), 147 (53.4), 132 (19.3), 120 (24.7), 118 (14.3), 117 (10.9), 91 (11.8).

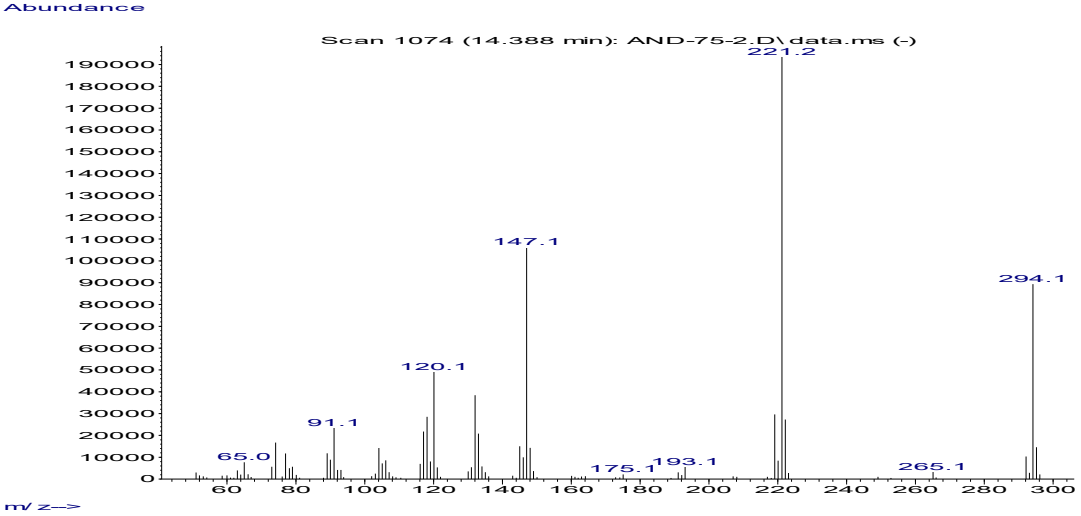


Figure S119. Mass spectrum (EI) of diethyl 2,2'-((2-methyl-1,3-phenylene)bis(azanediyl))diacetate **7ss**.

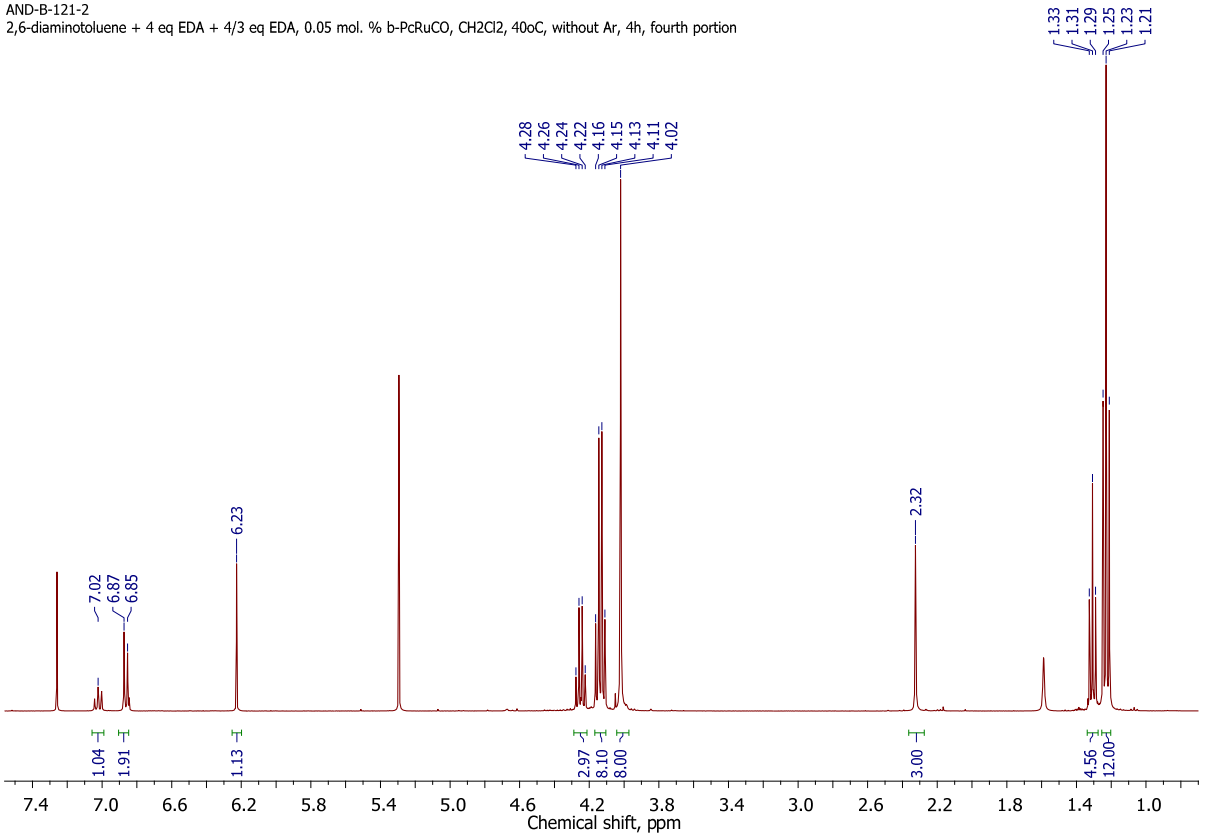


Figure S120. ^{1}H NMR spectrum of the reaction mixture after reaction of 2-methylbenzene-1,3-diamine **7** with 4 equiv. EDA in the presence of 0.05 mol. % **1β**.

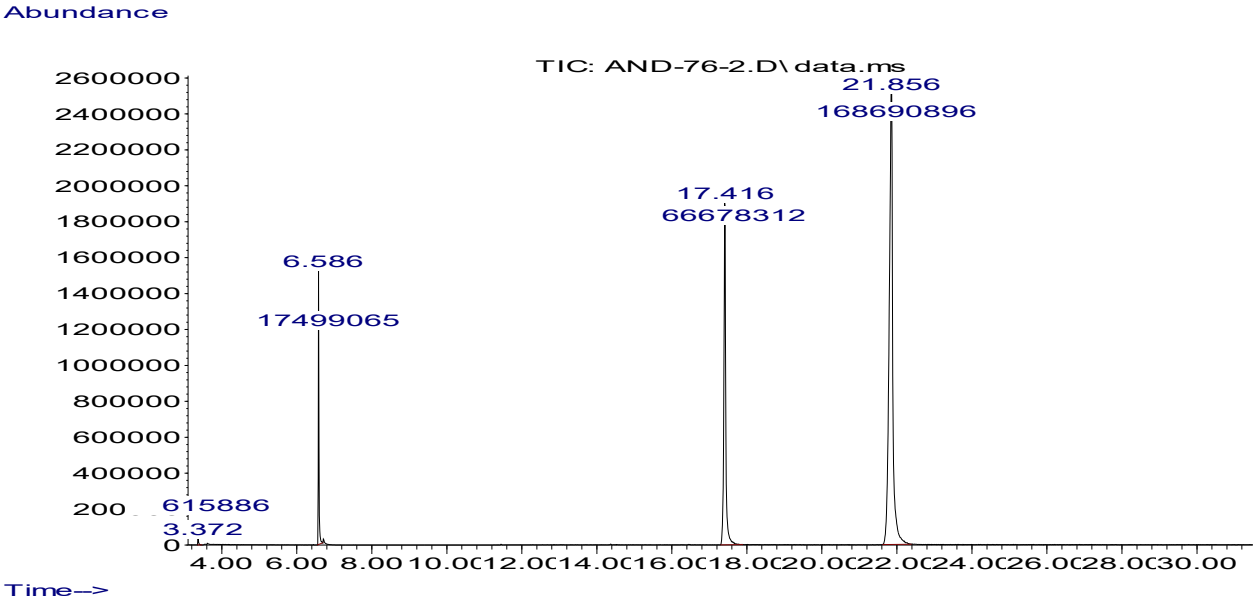
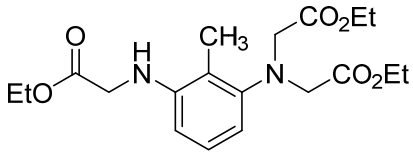


Figure S121. Chromatogram of the reaction mixture after reaction of 2-methylbenzene-1,3-diamine **7** with 4 equiv. EDA in the presence of 0.05 mol. % **1β**.

Diethyl 2,2'-((3-((2-ethoxy-2-oxoethyl)amino)-2-methylphenyl)azanediyl)diacetate, 7sd



MS (EI) m/z (%): 380 (13.1), 308 (19.0), 307 (100), 233 (12.1), 161 (9.0), 147 (17.4), 146 (7.3), 132 (8.1), 117 (7.2), 91 (6.0).

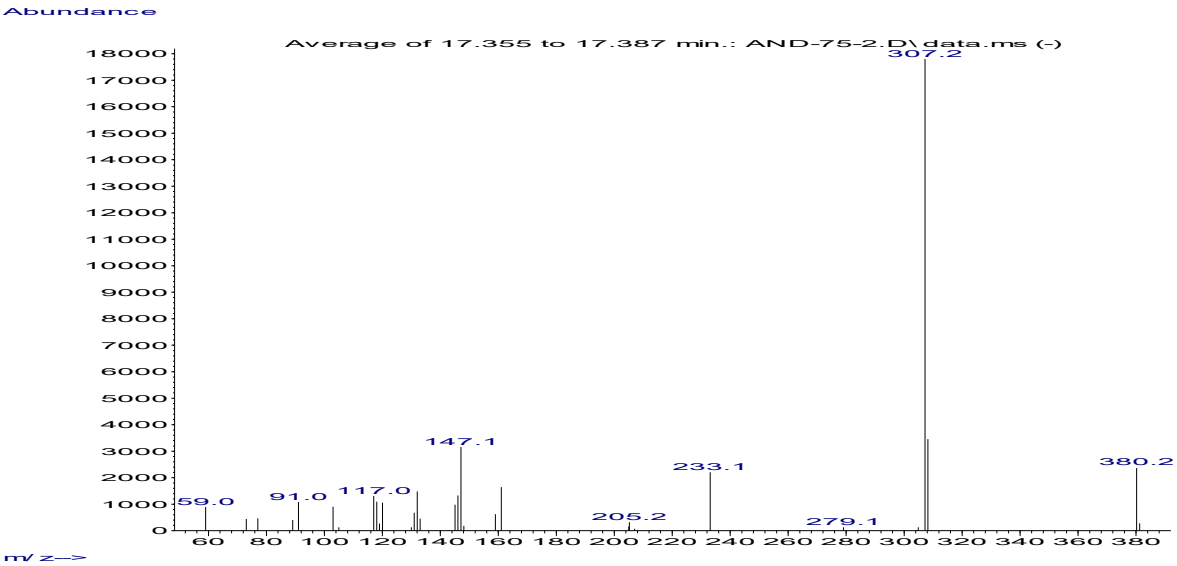


Figure S122. Mass spectrum (EI) of diethyl 2,2'-((3-((2-ethoxy-2-oxoethyl)amino)-2-methylphenyl)azanediyl)diacetate **7sd**.

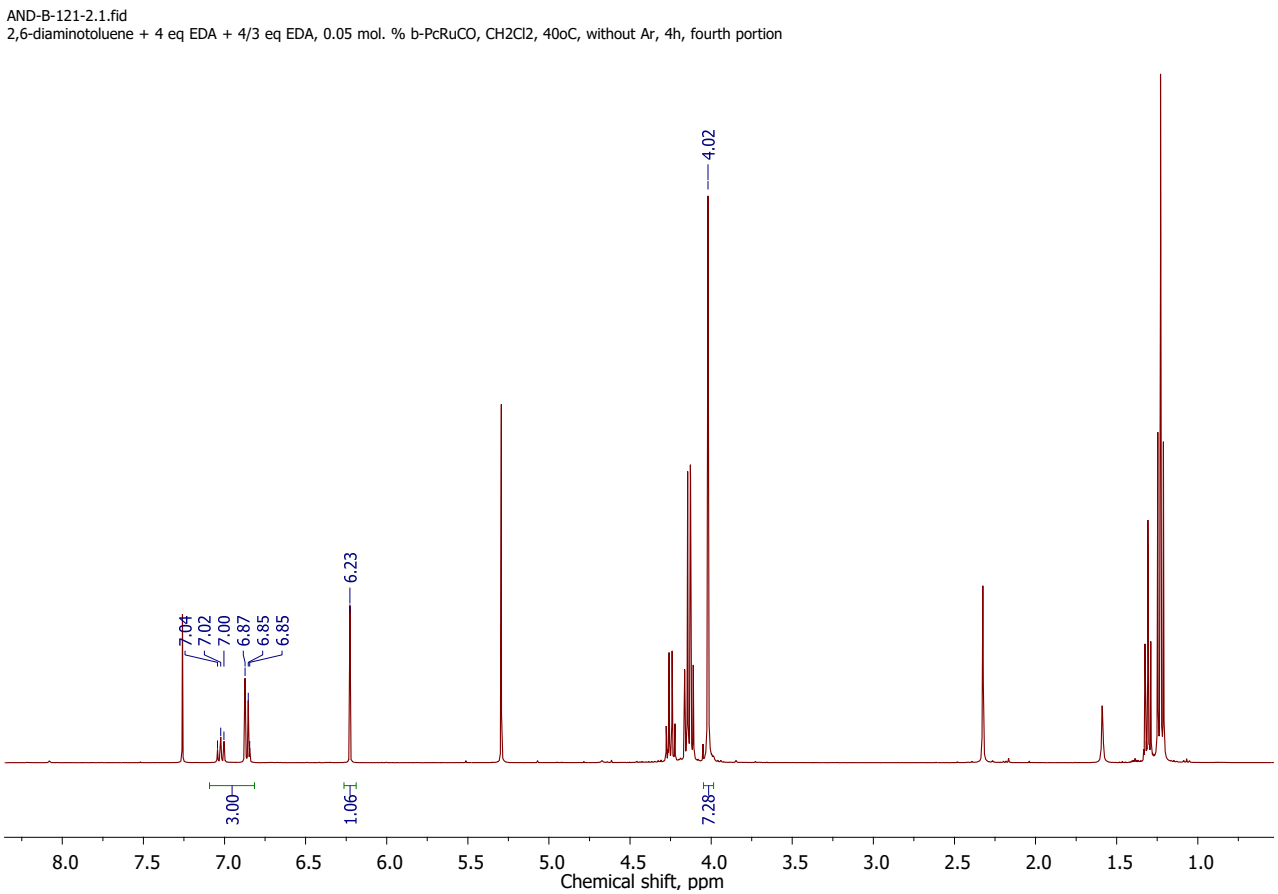
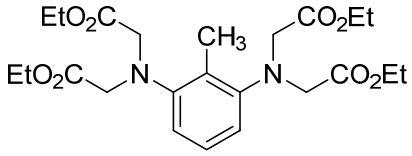


Figure S123. ^{1}H NMR spectrum of the reaction mixture after reaction of 2-methylbenzene-1,3-diamine **7** with 5.46 equiv. EDA in the presence of 0.05 mol. % **1β**.

Tetraethyl 2,2',2'',2'''-((2-methyl-1,3-phenylene)bis(azanetriyl))tetraacetate 7dd



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.99 – 6.92 (m, 1H), 6.80 (d, J = 8.0 Hz, 2H), 4.07 (q, J = 7.1 Hz, 8H), 3.95 (s, 8H), 2.26 (s, 3H), 1.16 (t, J = 7.1 Hz, 12H).

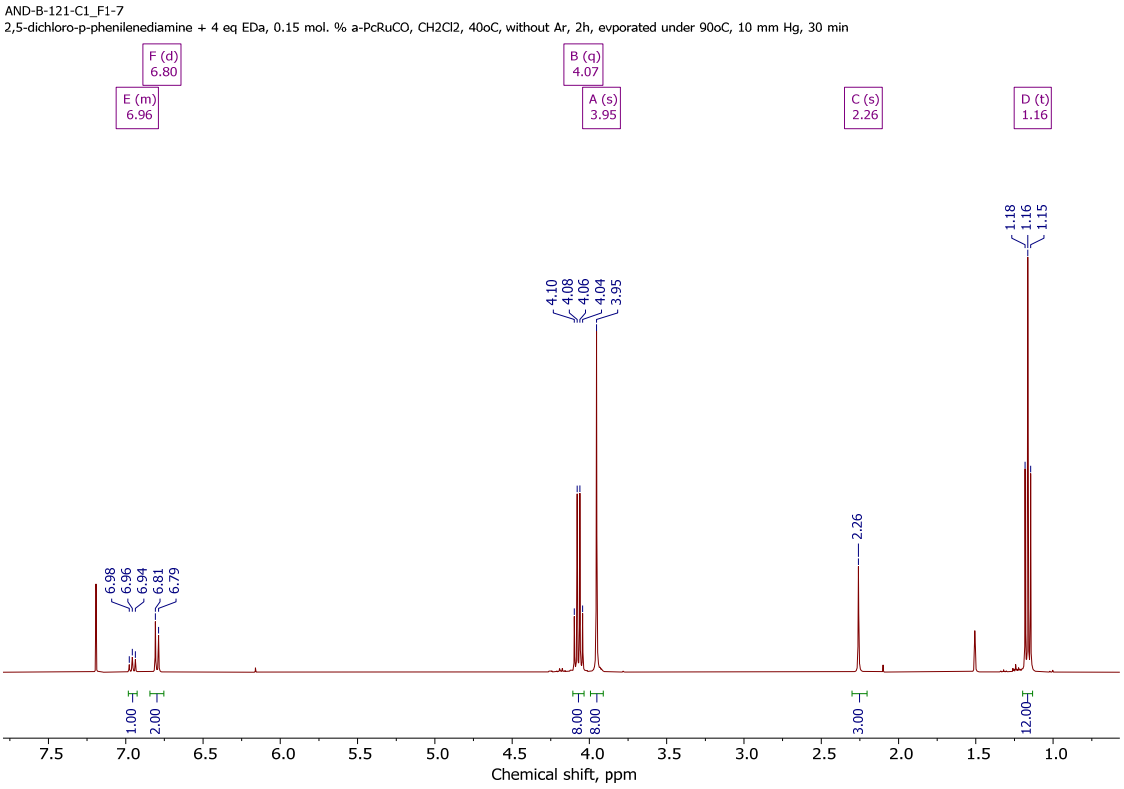


Figure S124. ^{1}H NMR spectrum of tetraethyl 2,2',2'',2'''-((2-methyl-1,3-phenylene)bis(azanetriyl))tetraacetate **7dd**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 171.23, 150.50, 127.71, 125.97, 117.71, 60.58, 54.25, 14.17, 13.97.

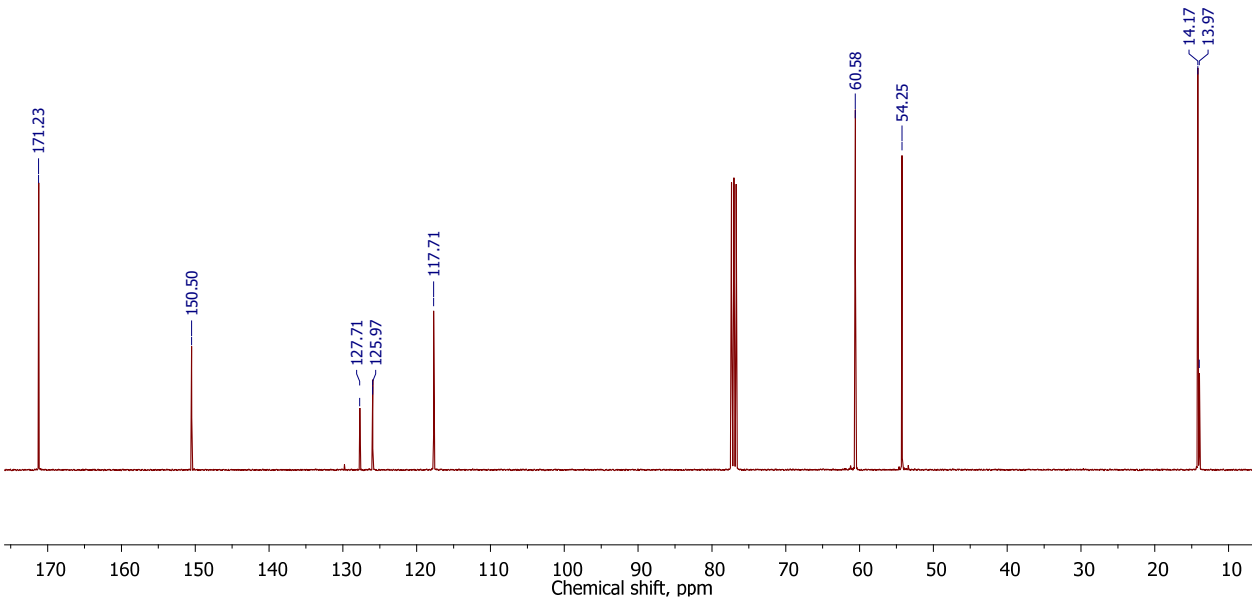


Figure S125. ^{13}C NMR spectrum of tetraethyl 2,2',2",2"'-((2-methyl-1,3-phenylene)bis(azanetriyl))tetraacetate **7dd**.

MS (EI) m/z (%): 466 (8.1), 394 (23.1), 393 (100), 233 (10.5), 160 (7.1), 159 (6.4), 146 (6.8), 132 (7.6), 117 (6.2), 59 (9.0).

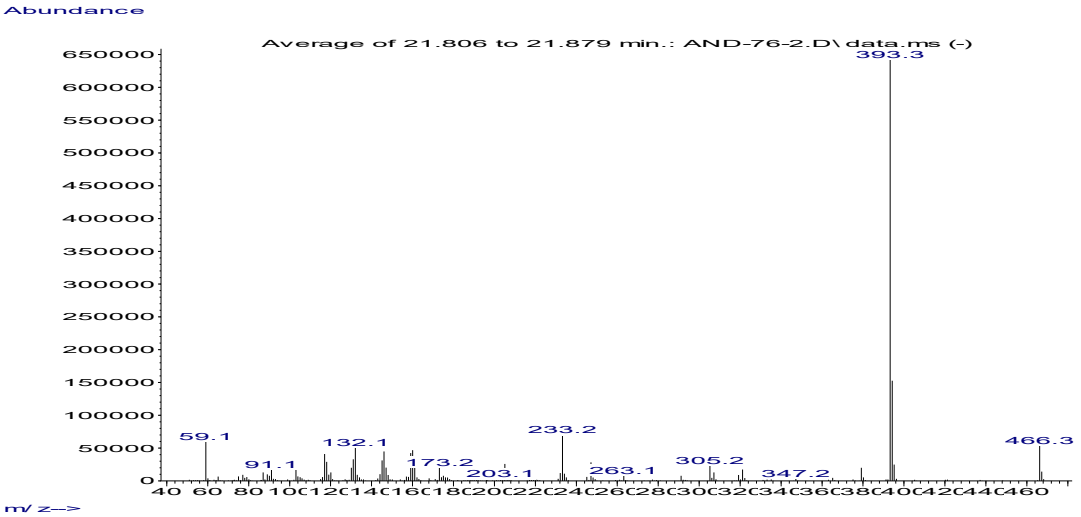


Figure S126. Mass spectrum (EI) of tetraethyl 2,2',2",2"'-((2-methyl-1,3-phenylene)bis(azanetriyl))tetraacetate **7dd**.

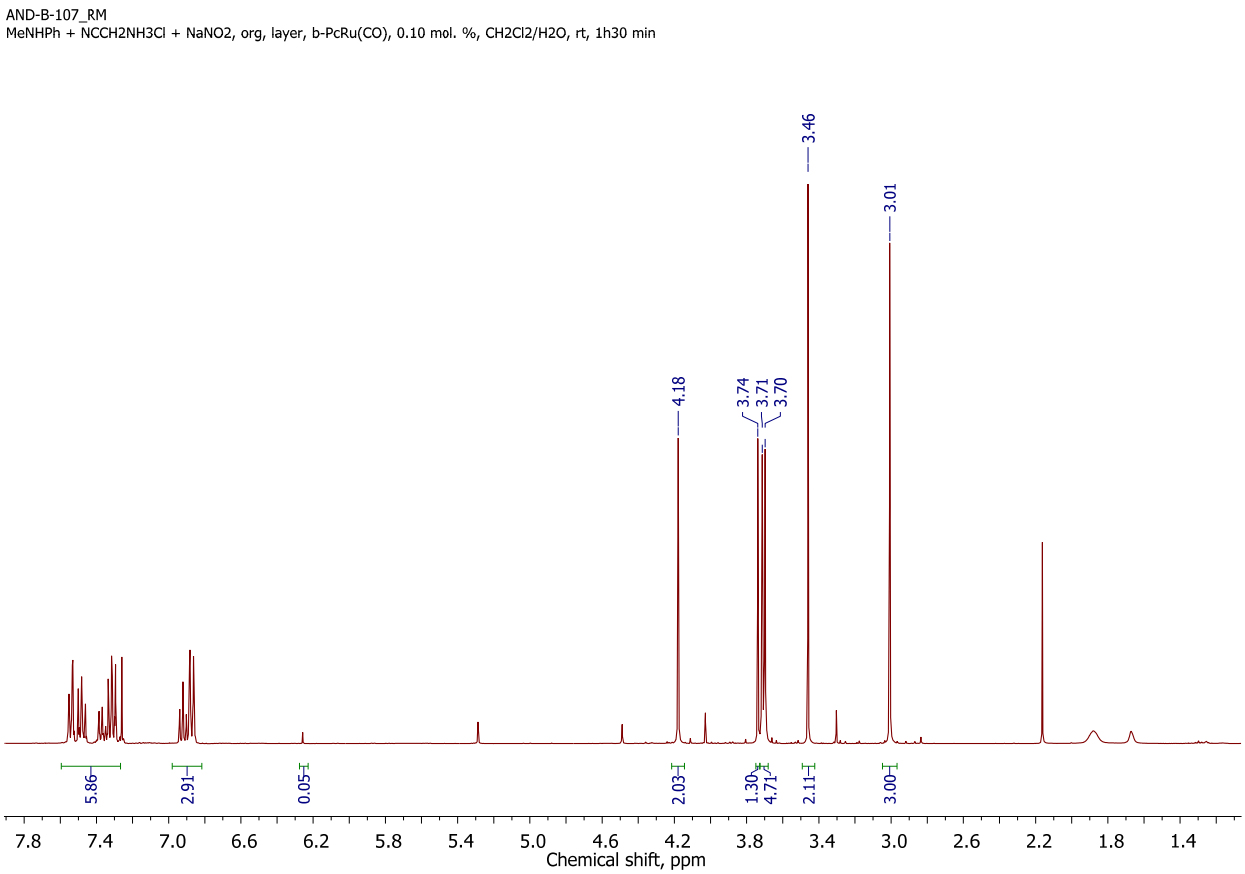


Figure S127. ^{1}H NMR spectrum of the organic phase after extraction of the reaction mixture from the reaction of N-methylaniline **8** with diazoacetonirile (generated in situ) in the presence of 0.1 mol. % **1β** in CH_2Cl_2/H_2O emulsion.

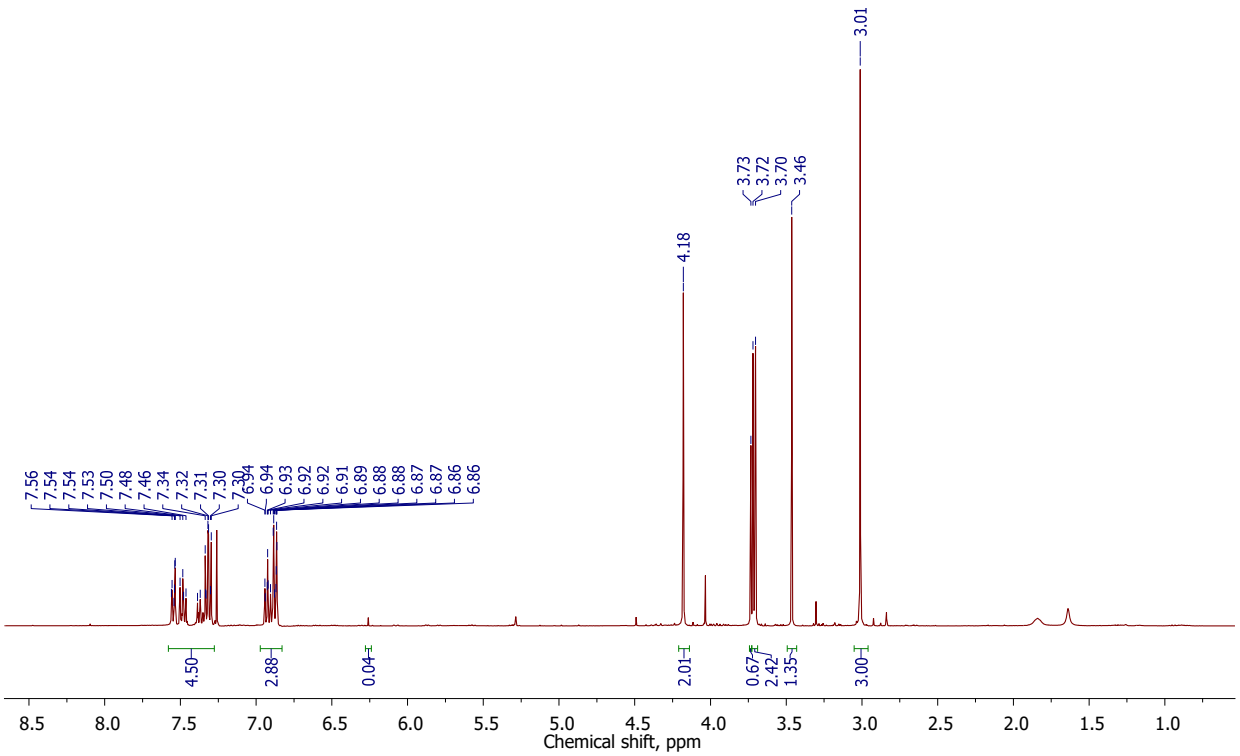


Figure S128. ^{1}H NMR spectrum of the organic phase after extraction of the reaction mixture from the reaction of N-methylaniline **8** with diazoacetonirile (generated in situ) in the presence of 0.1 mol. % **1β** in toluene/H_2O emulsion.

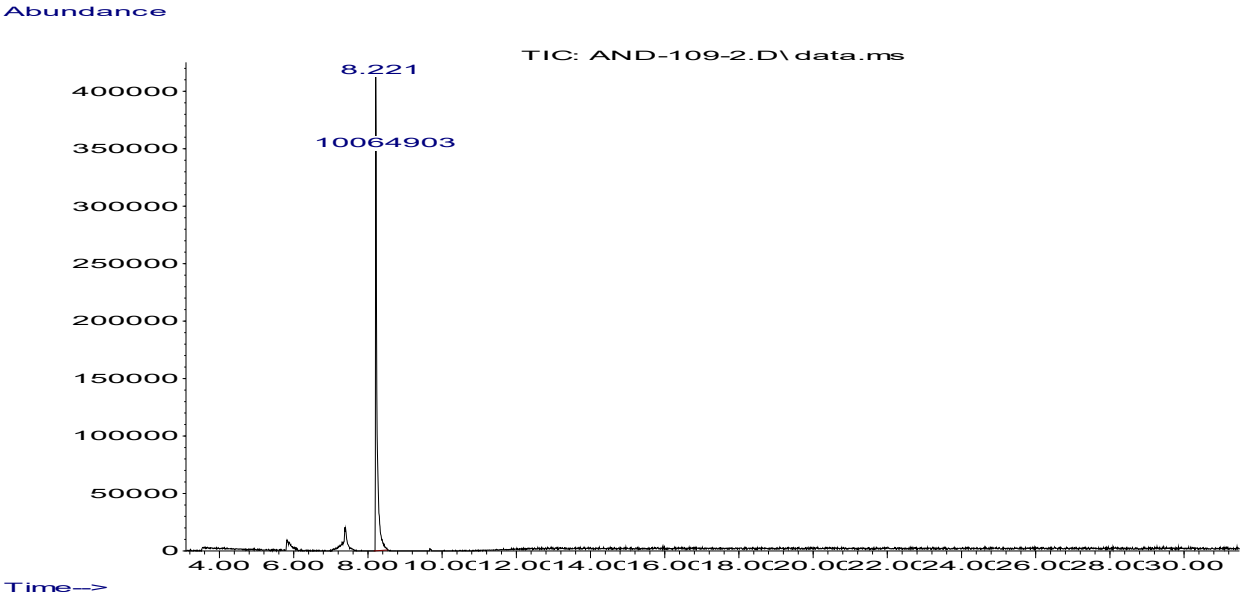


Figure S129. Chromatogram of the organic phase after extraction of the reaction mixture from the reaction of N-methylaniline **8** with diazoacetonirile (generated in situ) in the presence of 0.1 mol. % **1β** in toluene/H_2O emulsion.

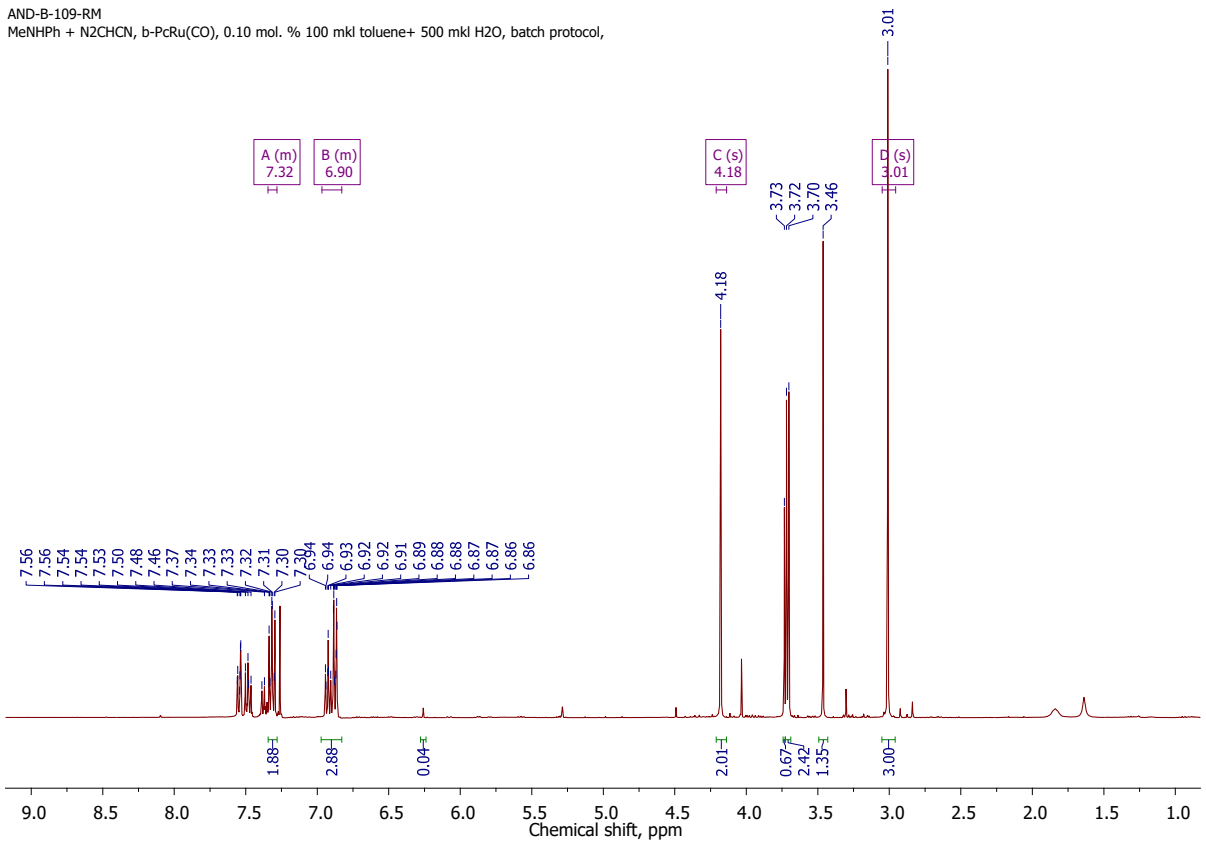


Figure S130. ^{1}H NMR spectrum of the reaction mixture after reaction of N-methylaniline **8** with diazoacetonitrile in $C_2H_4Cl_2$ (0.57 M) in the presence of 0.05 mol. % **1β**.

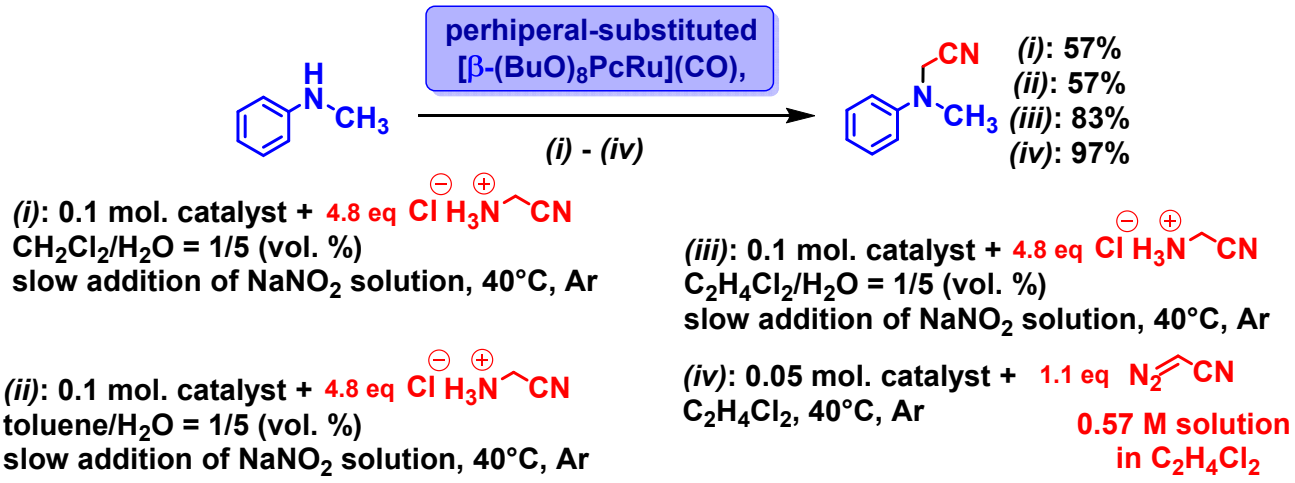
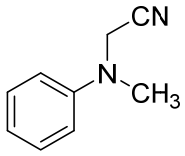


Figure S131. Optimization of the conditions of reaction of N-methylaniline **8** with diazo acetonitrile in the presence of **1β**.

2-(methyl(phenyl)amino)acetonitrile 9



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34 – 7.28 (m, 2H), 6.97 – 6.83 (m, 3H), 4.18 (s, 2H), 3.01 (s, 3H).

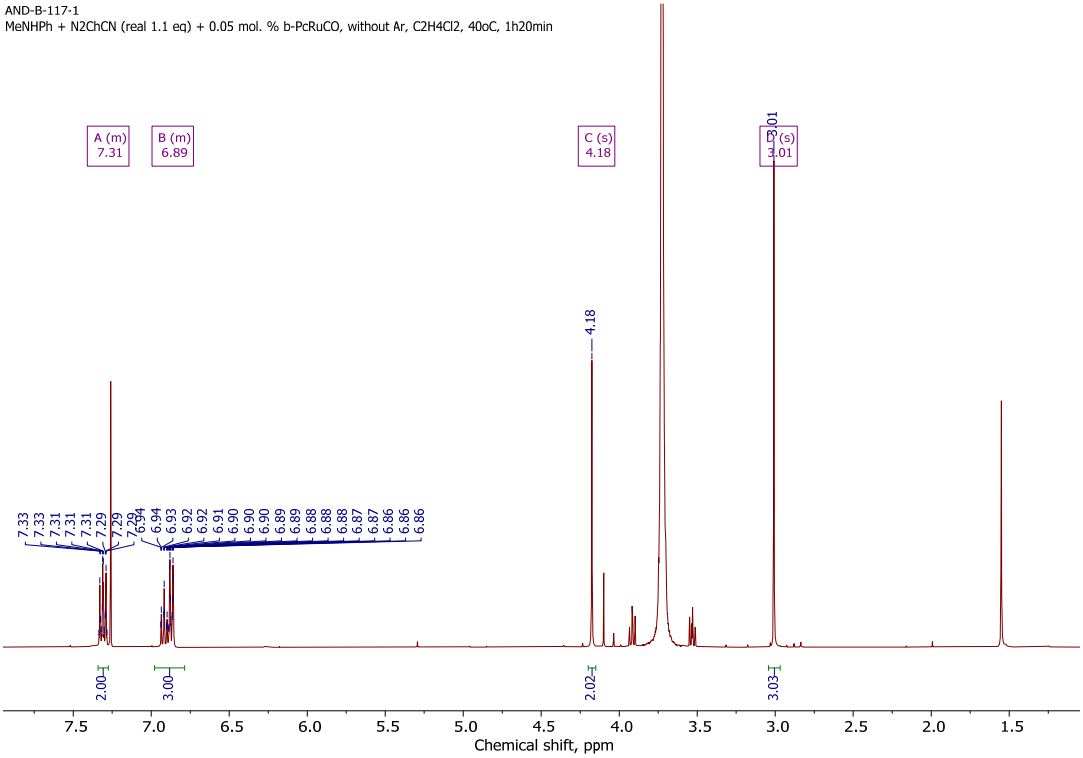


Figure S132. ^{1}H NMR spectrum of the crude 2-(methyl(phenyl)amino)acetonitrile **9** which is identical with the ^{1}H NMR spectrum of this product previously reported. S.-I. Murahashi, N. Komiya, H. Terai, and T. Nakae, *J. Am. Chem. Soc.* 2003, **125**, 15312–15313.

MS (EI) m/z (%): 146 (100), 145 (67.3), 120 (38.2), 106 (31.6), 105 (31.9), 104 (27.4), 79 (12.5), 78 (17.6), 77 (51.7), 51 (18.1).

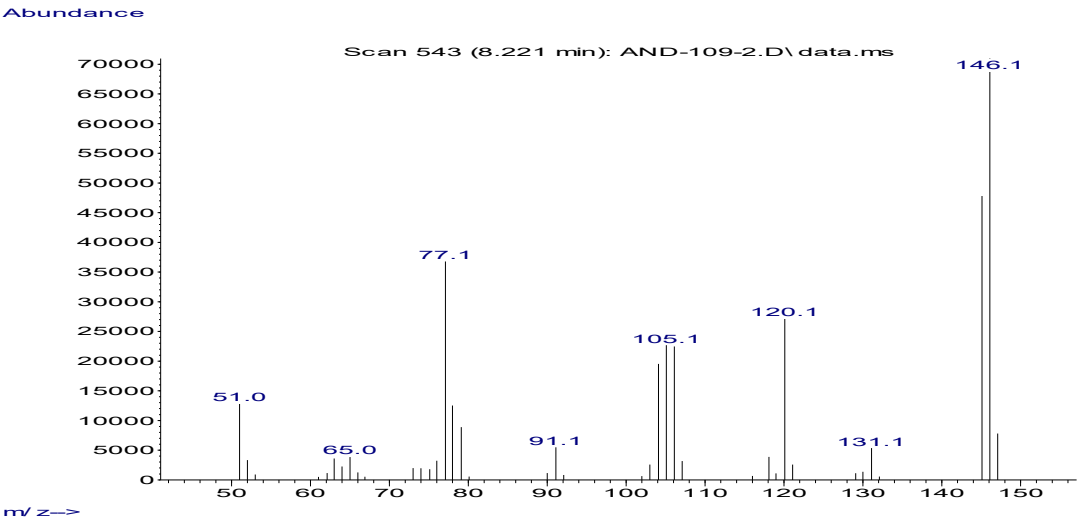
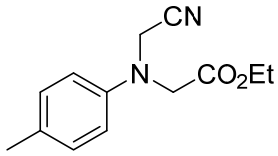


Figure S133. Mass spectrum (EI) of 2-(methyl(phenyl)amino)acetonitrile **9**.

Ethyl N-(cyanomethyl)-N-(p-tolyl)glycinate, 10



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.11 (d, J = 8.3 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 4.29 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.07 (s, 2H), 2.28 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

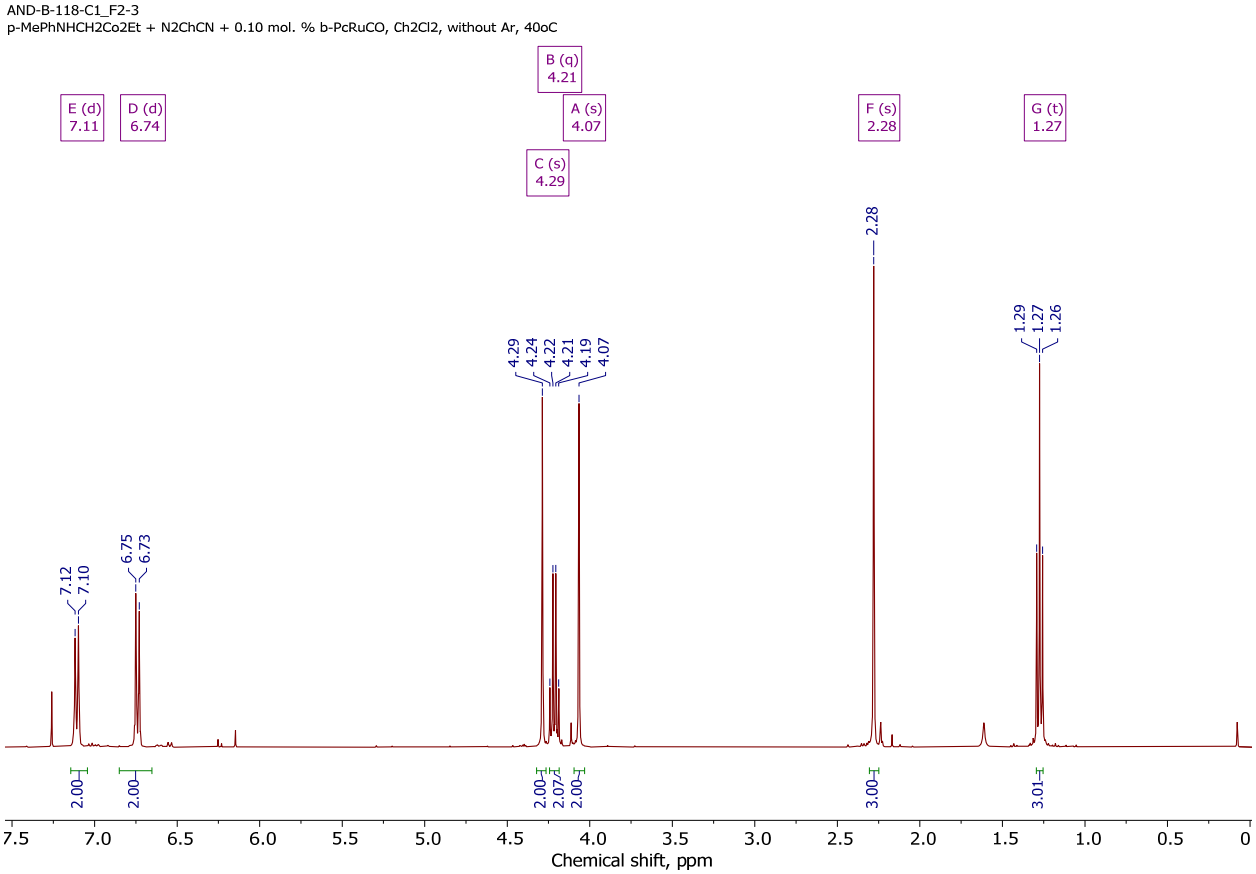


Figure S134. ^{1}H NMR spectrum of ethyl N-(cyanomethyl)-N-(*p*-tolyl)glycinate **10**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 170.01, 144.51, 130.11, 115.98, 114.91, 61.40, 53.27, 41.06, 20.37, 14.17.

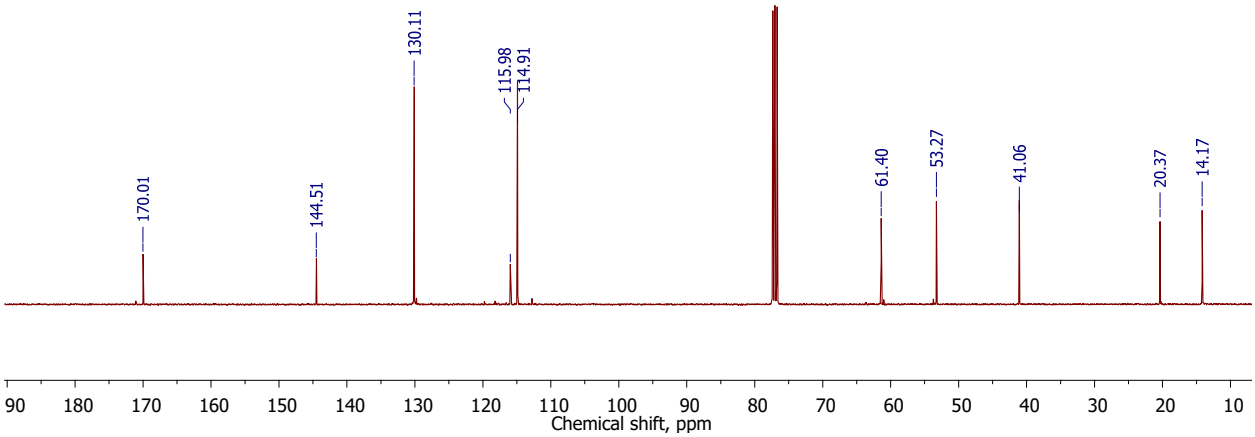


Figure S135. ^{13}C NMR spectrum of ethyl N-(cyanomethyl)-N-(*p*-tolyl)glycinate **10**.

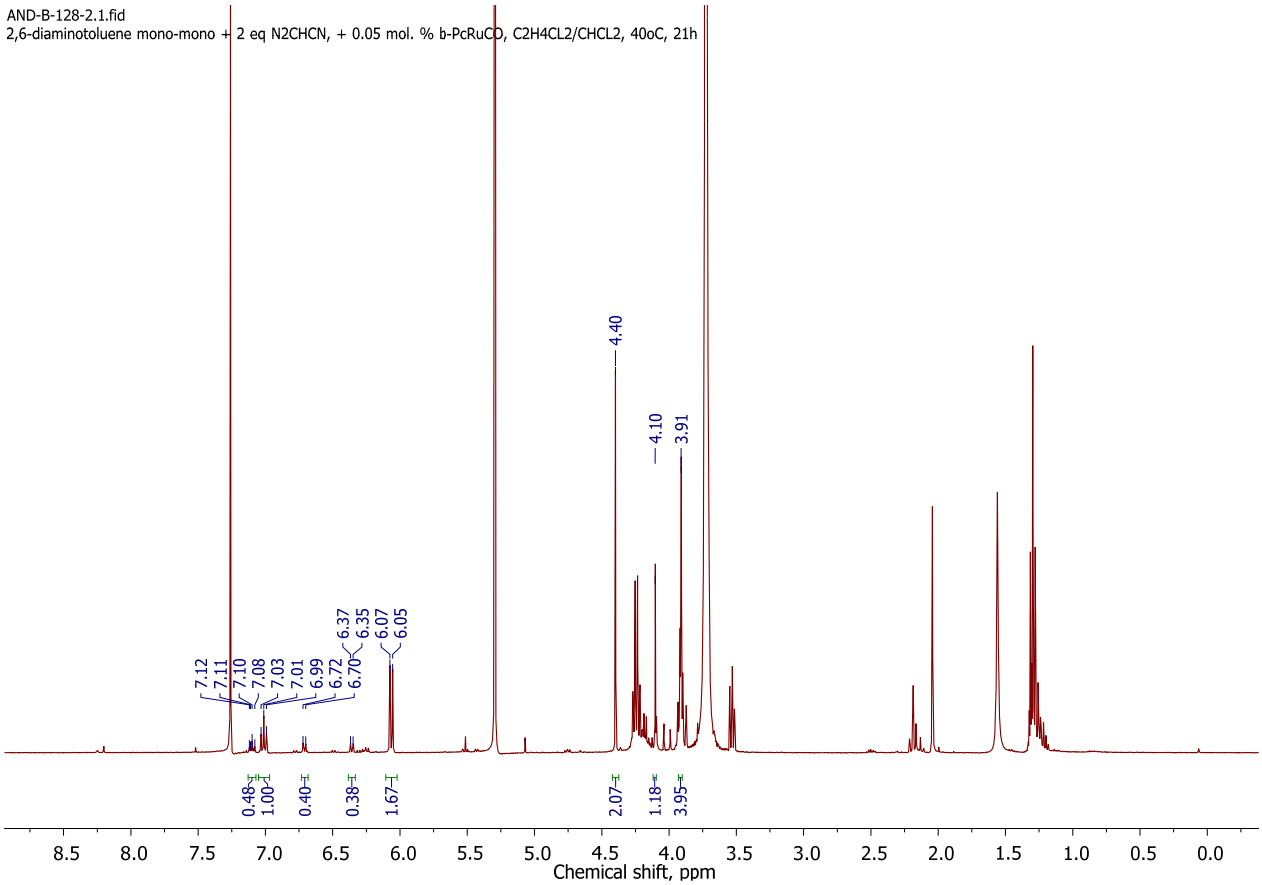


Figure S136. ^{1}H NMR spectrum of the reaction mixture after reaction of diethyl 2,2'-((2-methyl-1,3-phenylene)bis(azanediyl))diacetate **7ss** with 2.1 eq. diazoacetonitrile in $C_2H_4Cl_2$ (0.57 M) in the presence of 0.05 mol. % **1β**.

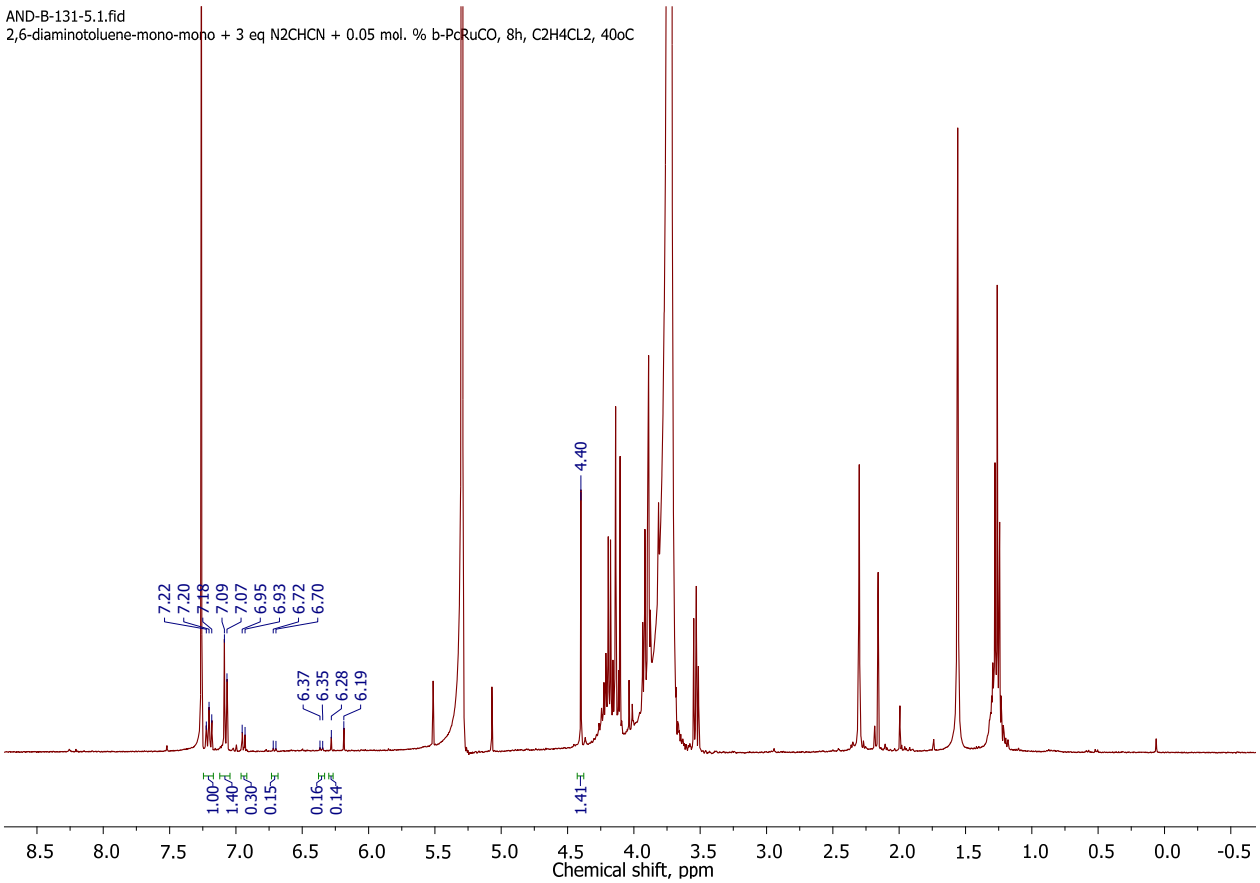


Figure S137. ^{1}H NMR spectrum of the reaction mixture after reaction of diethyl 2,2'-((2-methyl-1,3-phenylene)bis(azanediyl))diacetate **7ss** with 2.1 eq. diazoacetonitrile in $C_2H_4Cl_2$ (0.57 M) in the presence of 0.20 mol. % **1β**.

Ethyl (3-((cyanomethyl)(2-ethoxy-2-oxoethyl)amino)-2-methylphenyl)glycinate

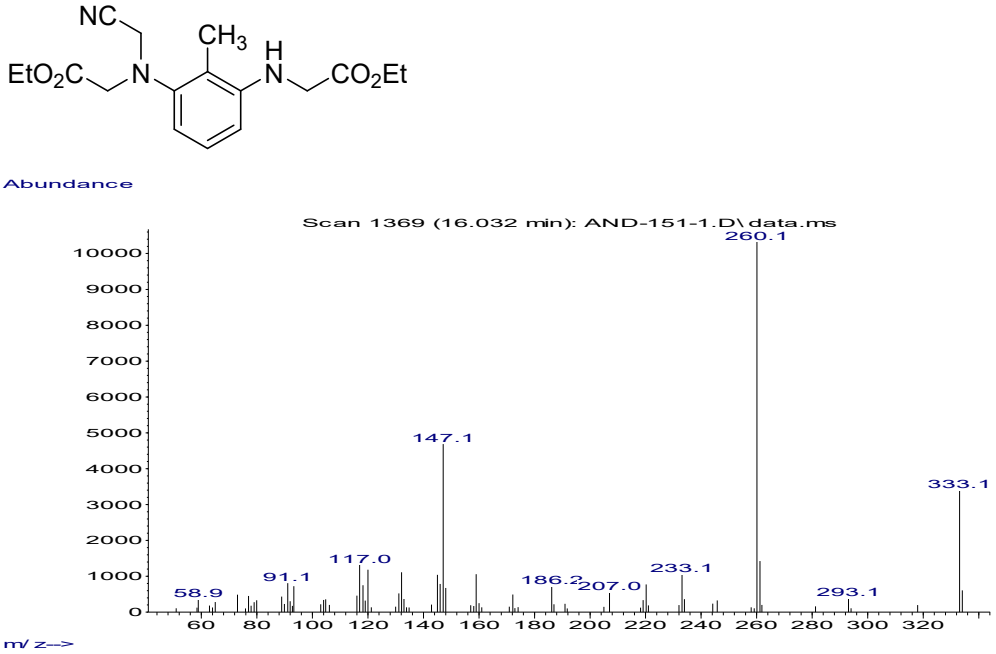
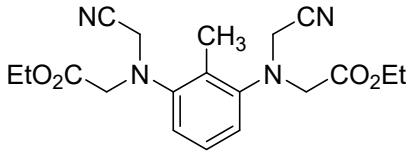


Figure S138. Mass spectrum (EI) of ethyl (3-((cyanomethyl)(2-ethoxy-2-oxoethyl)amino)-2-methylphenyl)glycinate.

Diethyl 2,2'-((2-methyl-1,3-phenylene)bis((cyanomethyl)azanediyl))diacetate, 11



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.23 – 7.16 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 4.19 (q, J = 7.1 Hz, 5H), 4.14 (s, 2H), 3.89 (s, 3H), 2.31 (s, 4H), 1.27 (t, J = 7.1 Hz, 7H).

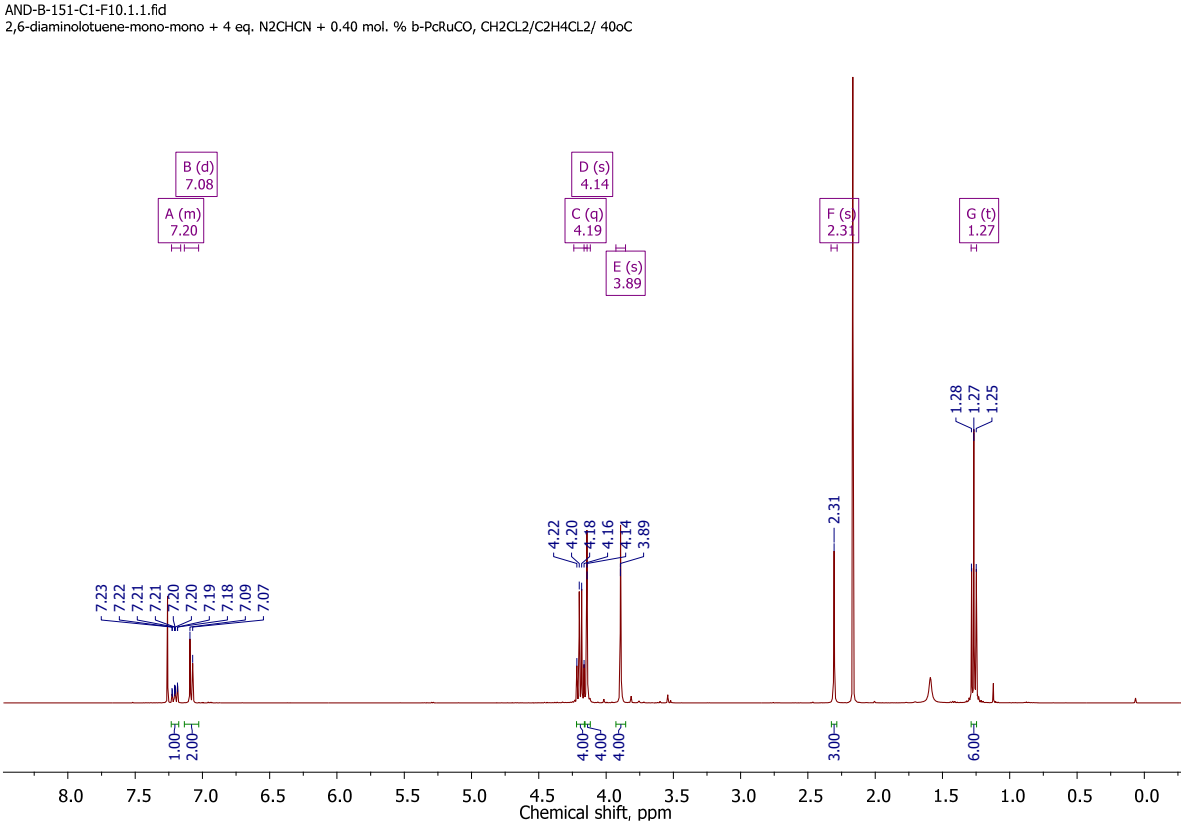


Figure S139. ^{1}H NMR spectrum of diethyl 2,2'-((2-methyl-1,3-phenylene)bis((cyanomethyl)azanediyl))diacetate **11**.

^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm): 169.69, 149.04, 129.55, 127.21, 119.50, 115.84, 61.17, 53.83, 42.49, 14.14, 12.91.

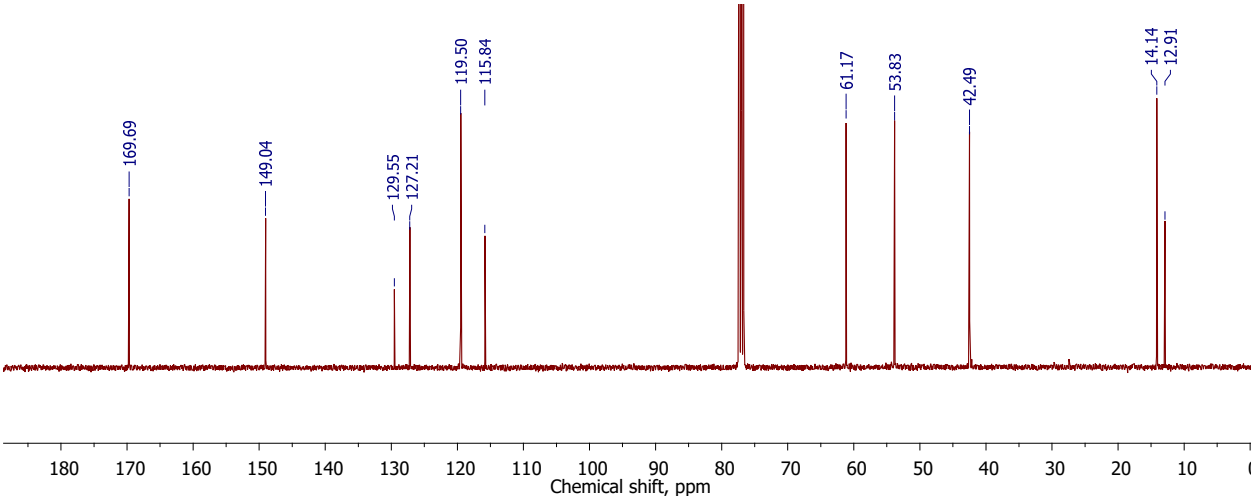


Figure S140. ^{13}C NMR spectrum of diethyl 2,2'-((2-methyl-1,3-phenylene)bis((cyanomethyl)azanediyl))diacetate **11**.

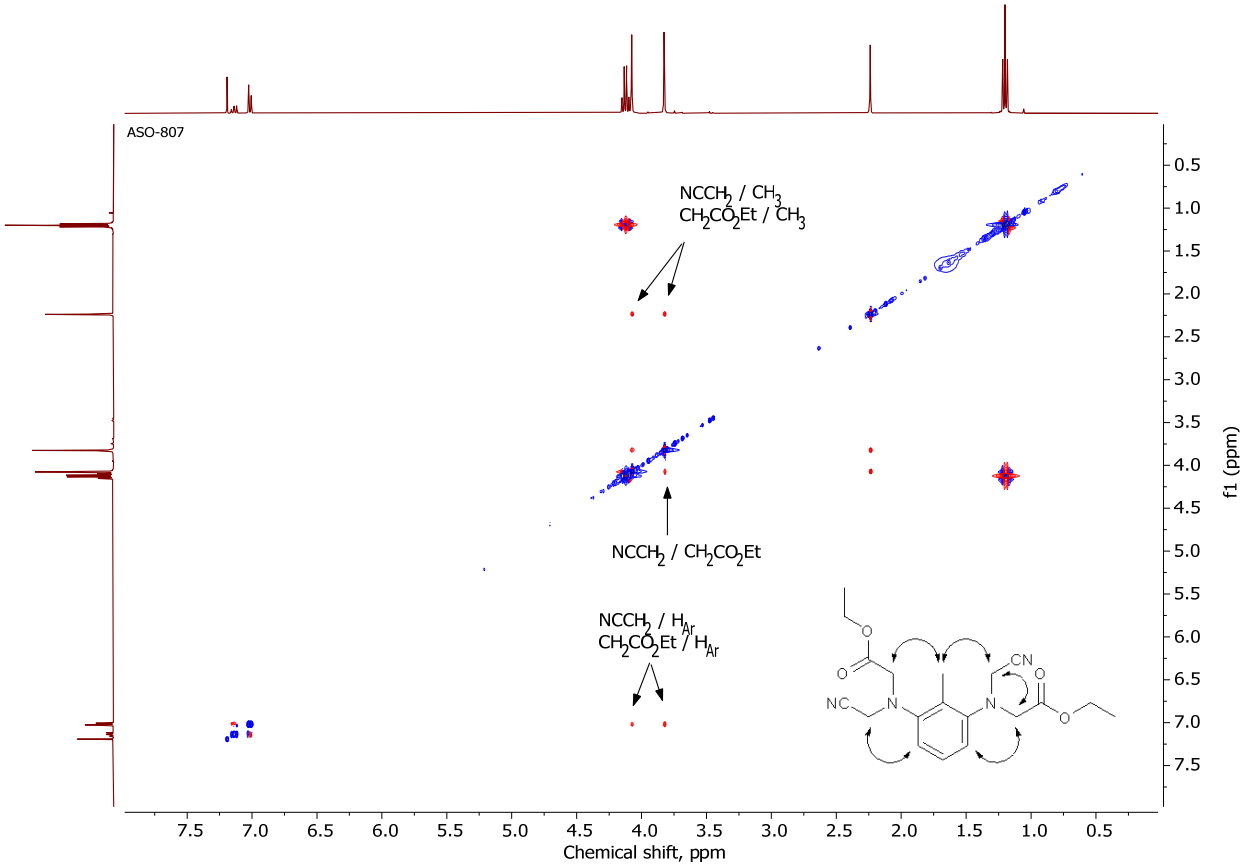


Figure S141. NOESY spectrum of diethyl 2,2'-((2-methyl-1,3-phenylene)bis((cyanomethyl)azanediyl))diacetate **11**.

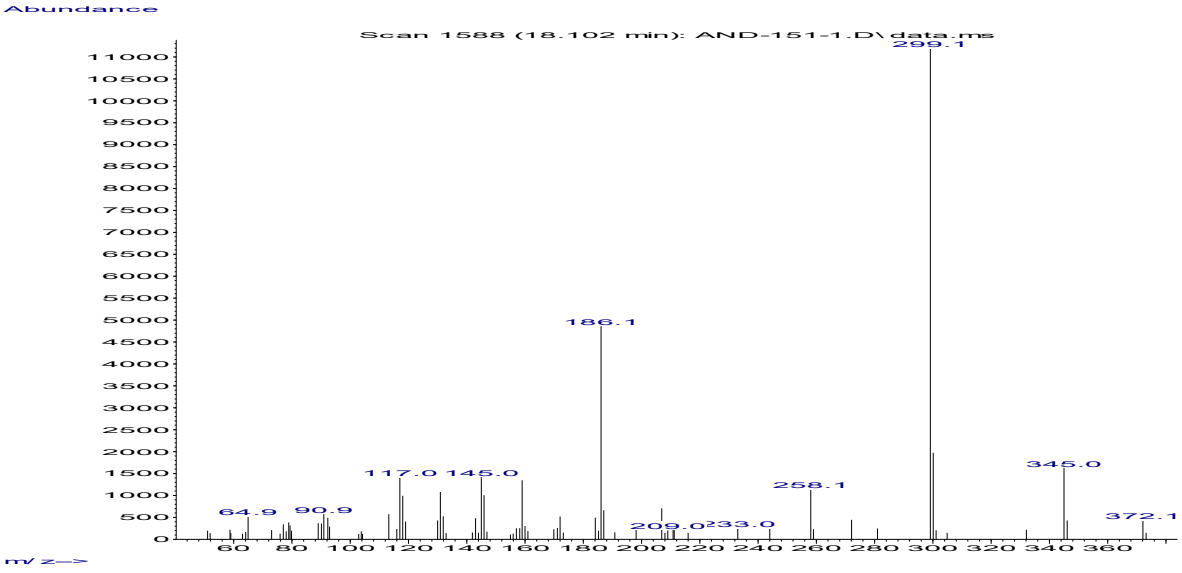


Figure S142. Mass spectrum (EI) of diethyl 2,2'-((2-methyl-1,3-phenylene)bis((cyanomethyl)azanediyl))diacetate **11**.