Experimental part

Starting materials

Unless otherwise noted, all reagents including ruthenium carbonyl (Sigma-Aldrich, 99 %), Ethyl diazoacetate (EDA, Sigma-Aldrich, containing ~ 13 wt % of dichloromethane), benzyl diazoacetate (BnDA, Sigma-Aldrich, containing ~ 10 wt % of dichloromethane), *tert*-butyl diazoacetate (*t*BuDA, Sigma-Aldrich, containing ~ 10 wt % of dichloromethane), amines, *o*-dichlorobenzene, hexane, diethylamine, methanol were purchased from commercial suppliers (Alfa Aesar, TCI, Sigma-Aldrich) and used without further purification. Chloroform was distilled and kept over $NaHCO_3$ to remove acidic impurities. The solution of 2,2,2-trifluorodiazoethane[1] and diazoacetonitrile[2,3] in dichloromethane was prepared according to the published procedures. Their concentrations were determined by ^1H NMR using standard (0.5 M DMSO solution in $CDCl_3$). 6,7-dibutoxynaphthalene-2,3-dicarbonitrile and 3,4,9,10,15,16,21,22-octabutoxynaphthalocyanine **H_2[(γ-BuO)$_8$Nc]** were synthesized according to the previously reported procedure.[4]

Methods

HRMS data were recorded 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 JASCO V-770 or Agilent 8453 diode-array spectrophotometers in the 250−900 nm range in rectangular quartz cuvette with 10 mm optical pathway. The NMR spectra were acquired on a Bruker Avance HD (400 MHz) or a Bruker Avance 600 spectrometers at 25°C. The NMR samples were prepared in $CDCl_3$ containing CD_3OD or pyridine-*d*$_5$ additives. $CDCl_3$ was filtered through an alumina layer prior to use, other deuterated solvents were used without further purification and kept in the dark in the freezer. The NMR spectra were referenced to the solvent signals.[5] The reaction products were identified by GC-MS technique using Hewlett Packard 5973/6890 system (electron impact at 70 eV, He carrier gas, 30 m × 0.25 mm x 0.25 μm Agilent J&W CycloSil-B column) and Agilent Technologies 5977B/7820A (electron impact at 70 eV, He carrier gas, Varian CP-Chirasil-Dex CB 25 m × 0.32 mm x 0.25 μm column).

3,4,9,10,15,16,21,22-octabutoxynaphthalocyaninatoruthenium(II) carbonyl, [(γ-BuO)$_8$NcRu](CO)

A 25 ml double-neck flask, equipped with magnetic stirring bar and reflux condenser, was charged with **H_2[(γ-BuO)$_8$Nc]** (32.0 mg, 24.8 μmol), $Ru_3(CO)_{12}$ (23.8 mg, 37.2 μmol) and 3 mL of *o*-dichlorobenzene. The mixture was degassed by three-times pumping and flushing with argon on the Schlenk line and then immersed in the bath at 190°C and refluxed for 35 min. The broad Q-bands in UV-vis spectrum at 713 and 783 nm ($CHCl_3$/MeOH mixture) of the starting naphthalocyanine disappeared and the Q-band of the metal complex appeared at 733 nm ($CHCl_3$). After cooling to room temperature the reaction was transferred onto column packed with SiO_2. Gradient elution with a mixture of *n*-hexane/chloroform (50 → 100 vol.%, + 0.5 vol. % Et_2NH) and chloroform/methanol (0 → 5 vol.%, + 0.5 vol. % Et_2NH) allowed to separate the ruthenium complex from unreacted naphthalocyanine. Further purification by size-exclusion chromatography on Bio-Beads SX-1 gel in $CHCl_3$ + 2.5 vol.% MeOH + 0.5 vol.% Et_2NH afforded the target ruthenium naphthalocyanine **[(γ-BuO)$_8$NcRu](CO)** as a dark-green solid (8.9 mg, 25%). **UV/vis** in CH_2Cl_2, λ_{max} /nm (lgε): 726 (5.05), 697 (4.60), 650 (4.52), 342 (5.00). UV/Vis in $C_2H_4Cl_2$, λ_{max} /nm (lgε): 726 (5.08), 697 (4.64), 650 (4.55), 342 (5.03). **^{1}H NMR** (600 MHz, $CDCl_3$ + 5 μl Py-d_5), δ: 9.51 (s, 1H, H_{Nc}), 7.71 (s, 1H, H_{Nc}), 4.44 – 4.12 (m, 4H, H_α), 2.08 – 1.95 (m, 4H, H_β), 1.72 – 1.60 (m, 4H, H_γ), 1.17 – 1.03 (m, 6H, H_{CH3}). **MALDI TOF MS**, *m/z*, DHB as the matrix, positive mode). Found: 2781.8, calculated for $[C_{160}H_{177}N_{16}O_{16}Ru_2]^+$ corresponding to $[M\text{-}CO]_2H^+$: 2782.2. Found: 1391.5, calculated for $[C_{80}H_{89}N_8O_8Ru]^+$ corresponding to $[M\text{-}CO]H^+$: 1391.6. **HR ESI**, *m/z*. Found: 1419.5789, calculated for $[C_{81}H_{88}N_8O_9Ru+H]^+$: 1419.5813.

Note 1: the reaction can also be carried out in refluxing benzonitrile under the same conditions.
Note 2: the starting naphthalocyanine **H_2[(γ-BuO)$_8$Nc]** is poorly soluble in $CHCl_3$. To record the UV-vis spectrum of the reaction mixture prior to heating, methanol was added to the cuvette. When the ruthenium complex formed the UV-vis spectrum of the reaction mixture can be registered in a pure $CHCl_3$.
Note 3: the addition of diethylamine during column purification allows for better separation and reduces the overlap between fractions containing unreacted ligand and those containing the target complex.
Note 4: in the absence of the matrix (DHB) the spectrum MALDI TOF of the ruthenium naphthalocyanine **[(γ-BuO)$_8$NcRu](CO)** did not change significantly.

Catalytic procedure for carbene insertion into N-H bonds.

Typical protocol: a 0.5 mL dichloroethane solution containing amine (1 M, 0.5 mmol, 1 eq.) and **[(γ-BuO)$_8$NcRu](CO)** (0.125 mM, $3.75 \cdot 10^{-5}$ mmol, 0.0125 mol %) was thoroughly bubbled with argon for 5 min and EDA (66 µl, 0.55 mmol, 1.1 eq.) was added at 40°C. The reaction mixture was stirred for 1- 4 hours. The resulting mixture was then analyzed by GC-MS, ^{1}H NMR ($CDCl_3$) ^{19}F NMR (for fluorine containing compounds). The substrate conversions and product yields were determined by ^{1}H NMR spectroscopy. The spectral data for the reaction products were identical to those previously described.

1 N. P. Ramirez, G. Pisella and J. Waser, *J. Org. Chem.*, 2021, **86**, 10928–10938.

2 A. L. Chandgude and R. Fasan, *Angew. Chem. Int. Ed.*, 2018, **57**, 15852–15856.

3 P. K. Mykhailiuk and R. M. Koenigs, *Chem. - Eur. J.*, 2020, **26**, 89–101.

4 A. G. Martynov, G. S. Berezhnoy, E. A. Safonova, M. A. Polovkova, Y. G. Gorbunova and A. Y. Tsivadze, *Macroheterocycles*, 2019, **12**, 75–81.

5 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

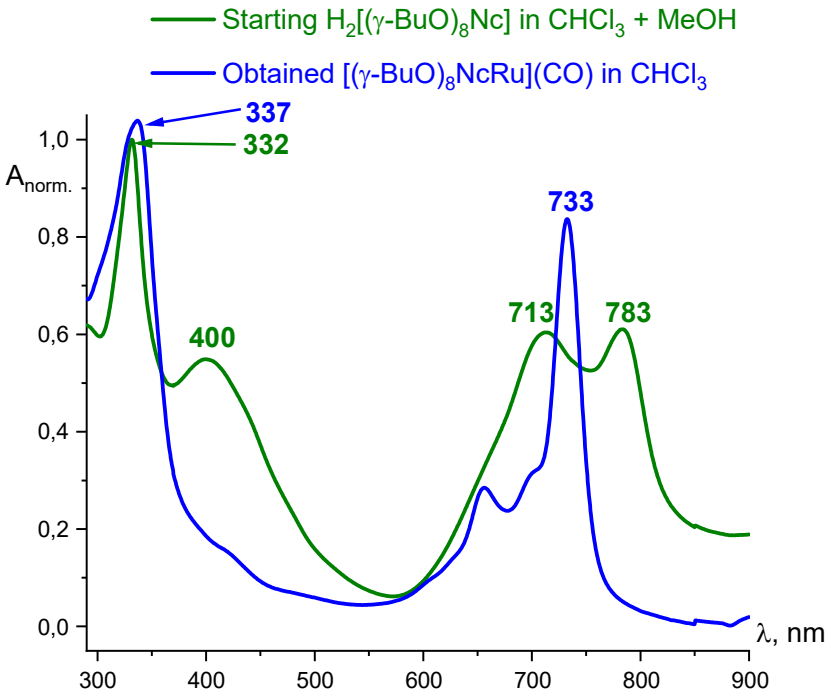


Fig. S1. *UV-Vis spectra of the reaction mixture containing the metal-free naphthalocyanine (in green) and obtained ruthenium complex (in blue) in the mixture of $CHCl_3$ and CH_3OH.*

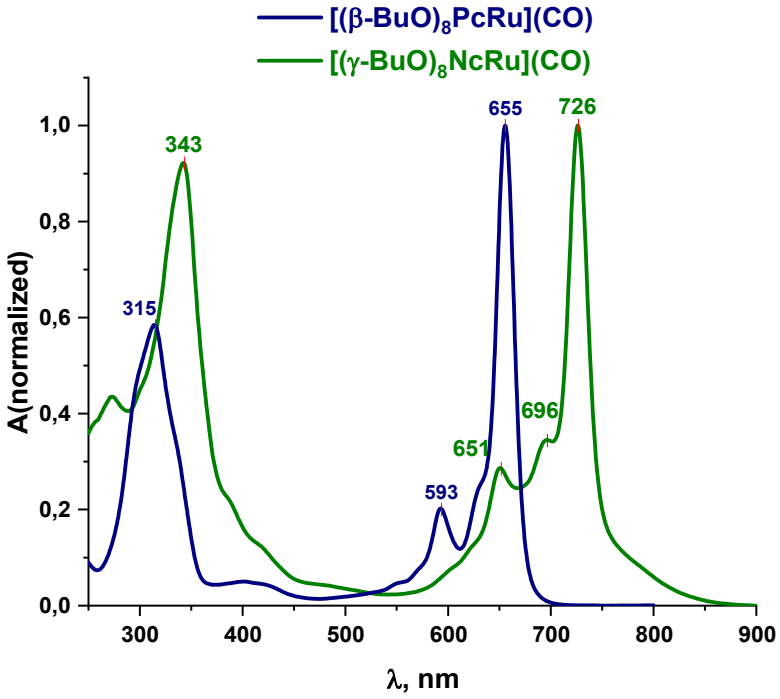


Fig. S2. *Comparison of the UV-Vis spectra of the ruthenium phthalocyanine* ***[(γ-BuO)$_8$PcRu](CO)*** *(blue line) and ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)*** *(green line) in CH_2Cl_2.*

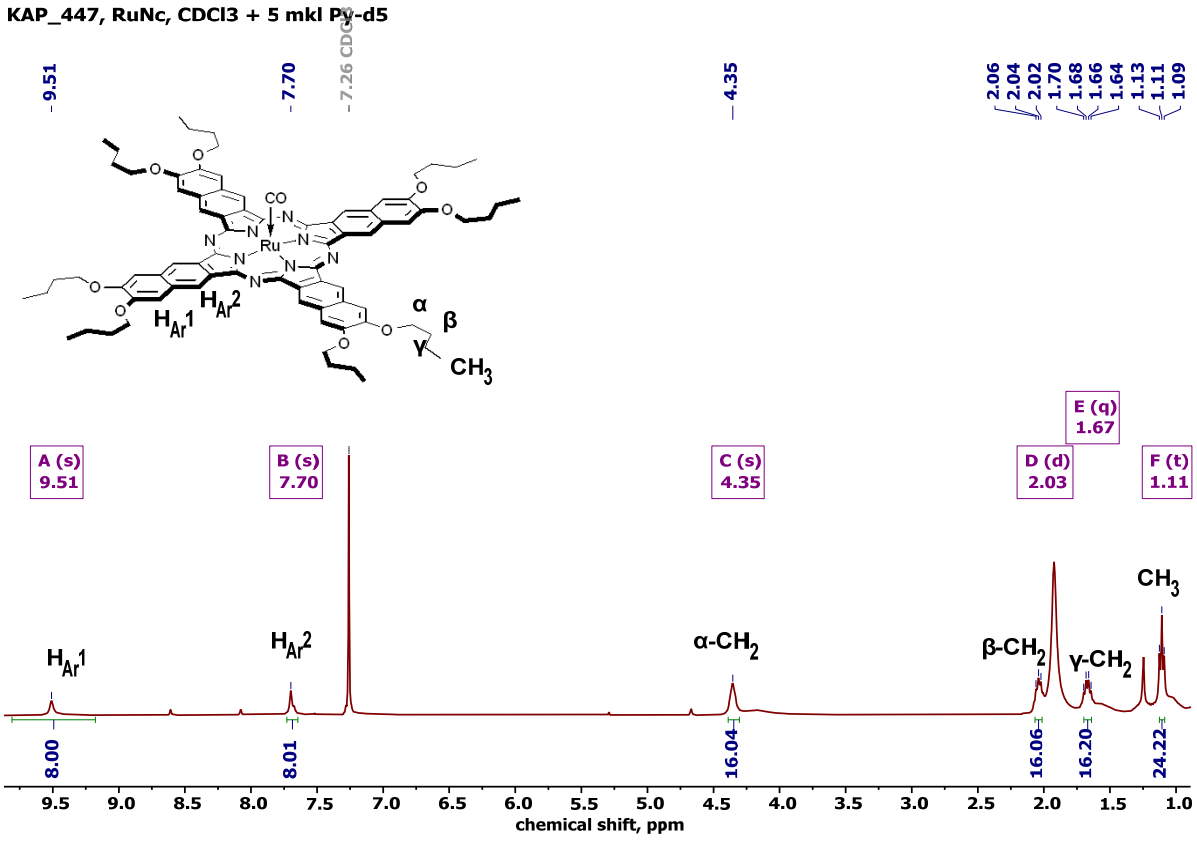


Fig. S3. *^{1}H NMR spectrum of the ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)*** *in $CDCl_3$ with addition of 5 μL Py-d_5.*

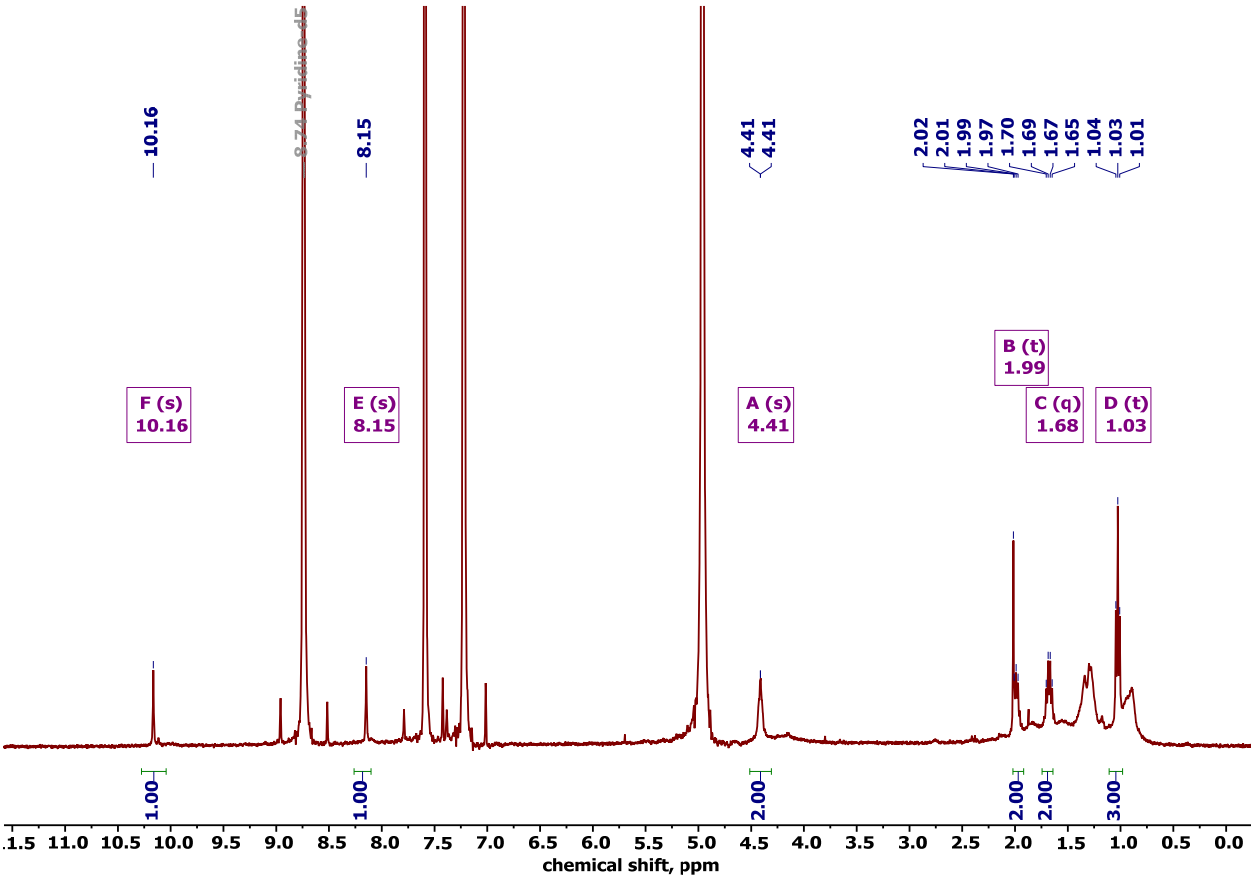


Fig. S4. *^{1}H NMR spectrum of the ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)*** *in Py-d_5.*

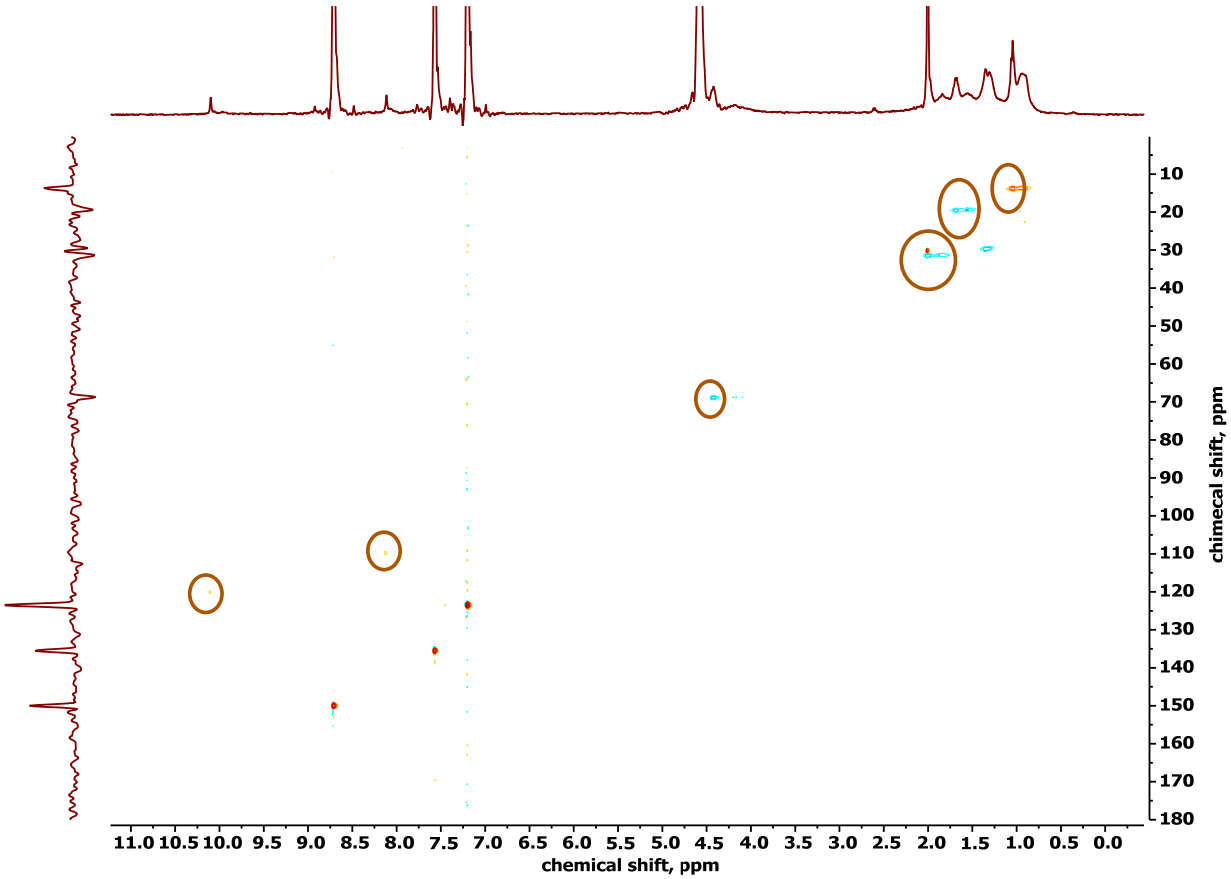


Fig. S5. *^{1}H-^{13}C HSQC spectrum of the the ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)*** *in Py-d$_5$ recorded at 50°C. Correlations are marked by circles.*

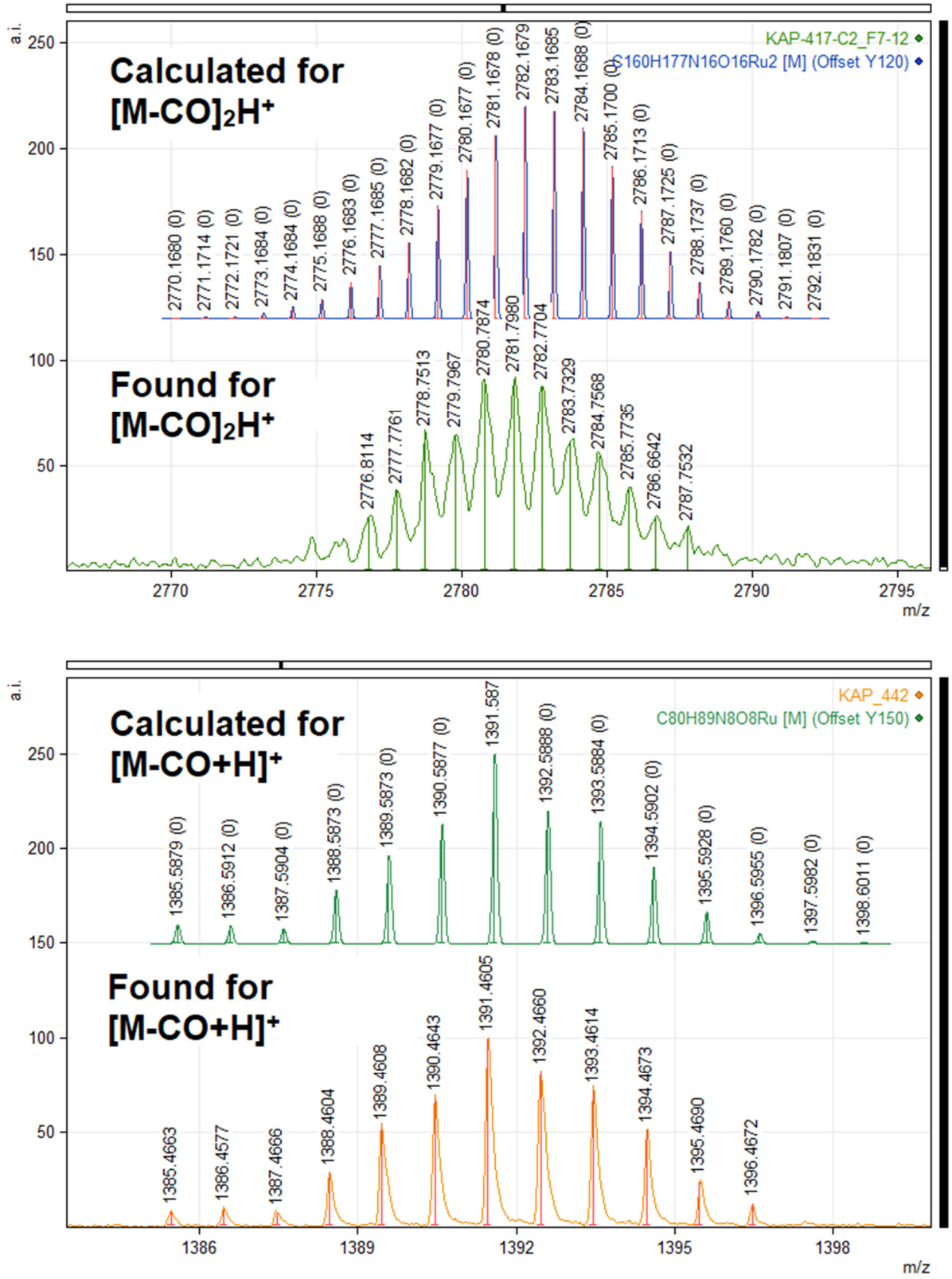


Fig. S6. *The MALDI TOF spectra of ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)***.

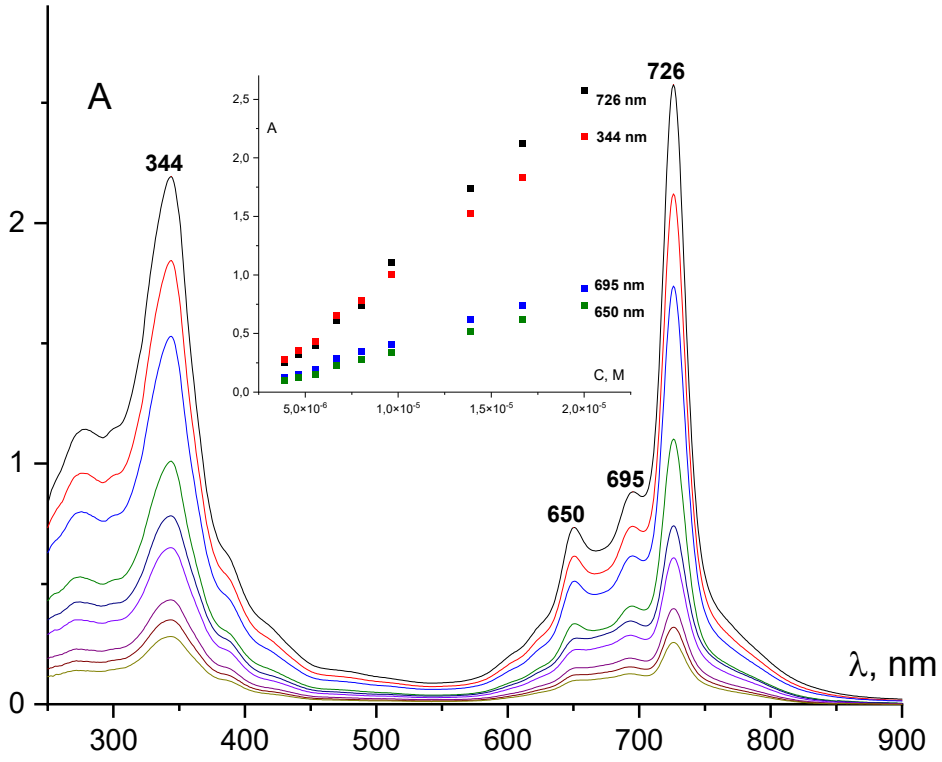


Fig. S7. *The concentration dependence of UV-vis spectra of ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)*** *in $C_2H_4Cl_2$.*

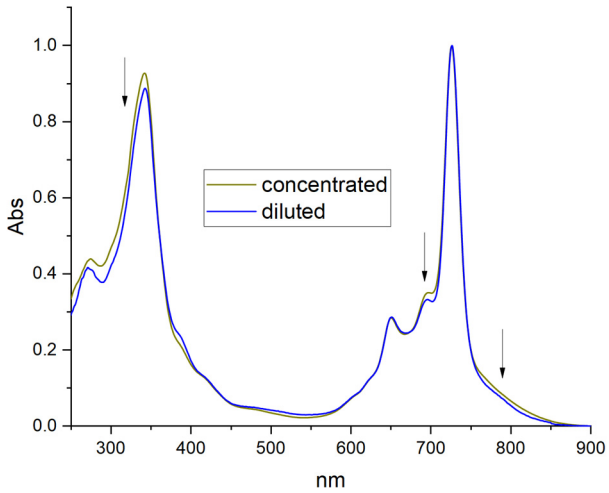


Fig. S8. *Comparison of normalized UV-vis spectra of ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)*** *in $C_2H_4Cl_2$ at 2 μM (in blue) and 20 μM (in grey) concentrations.*

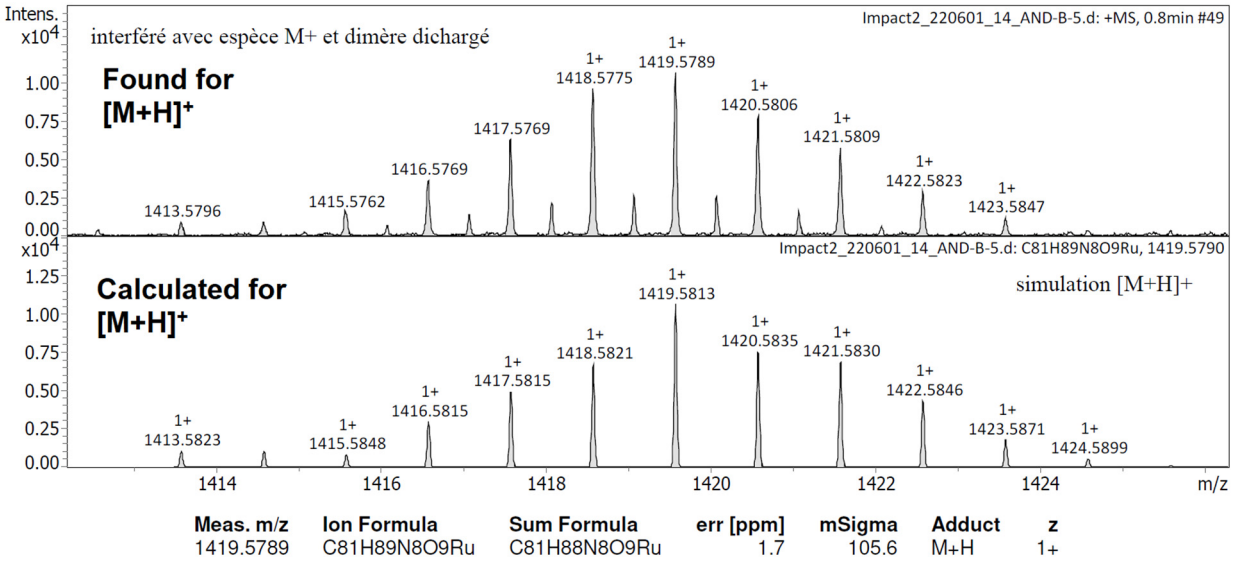


Fig. S9. *The HR ESI mass spectrum of ruthenium naphthalocyanine* ***[(γ-BuO)$_8$NcRu](CO)***.

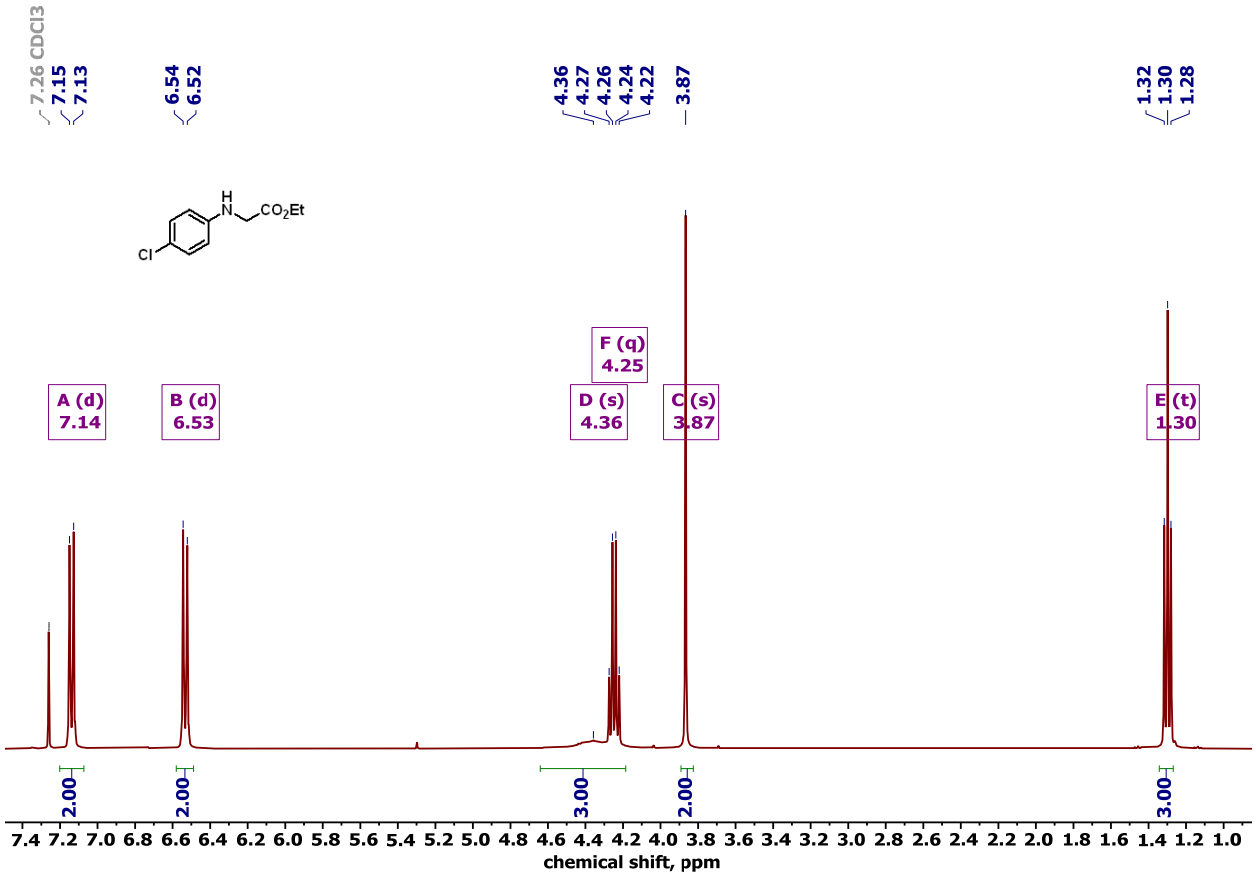
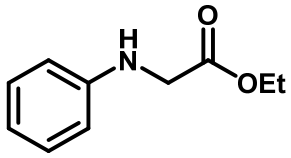


Fig. S10. *^{1}H NMR spectrum of isolated ethyl (4-chlorophenyl)glycinate after reaction of 10 mmol of p-chloroaniline with 11 mmol of ethyl diazoacetate in the presence of 0.0125 mol. %* ***[(γ-BuO)$_8$NcRu](CO)***.

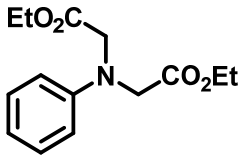
Characterization of the reaction products



N-phenylglycine ethyl ester was prepared from aniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.20 (t, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$), 8 ppm 14.18, 45.86, 60.29, 115.44, 128.26, 129.28, 145.81, 170.89. **MS (EI)** m/z (%): 179 (M^+, 19), 106 (100), 93 (1), 79 (6), 77 (22), 65 (1), 51 (8).

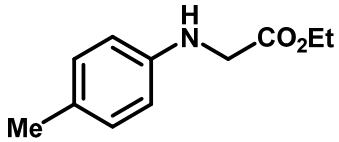
^{1}H NMR, **^{13}C NMR**: Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc*., 1996, **118**, 9901-9907.
MS (EI): A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



Diethyl 2,2'-(phenylazanediyl)diacetate was prepared from aniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 6.78 (t, J = 8.0 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 4.22 (q, J = 8.0 Hz, 4H), 4.14 (s, 4H), 1.28 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 148.0, 129.4, 118.4, 112.7, 61.2, 53.7, 14.4. **MS (EI)** m/z (%): 265 (M^+, 11), 193 (15), 192 (100), 120 (30), 106 (40), 105 (11), 104 (21), 91 (35), 77 (26), 59 (41).

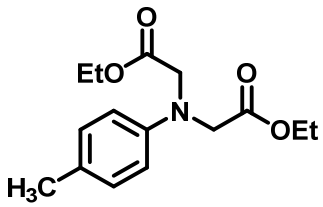
^{1}H NMR, **^{13}C NMR**: X. Xu, C. Li, Z. Tao and Y. Pan, *Adv. Synth. Catal.*, 2015, **357**, 3341-3345.
MS (EI): A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



N-(4-methylphenyl)glycine ethyl ester was prepared from *p*-toluidine and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.88 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDC1_3$), δ ppm 14.19, 20.33, 45.56, 60.27, 115.31, 129.47, 137.35, 143.96, 171.18. **MS (EI)** m/z (%): 193 (M^+, 18), 120 (100), 104 (1), 91 (19), 89 (4), 77 (3), 65 (8), 63 (2), 51 (2).

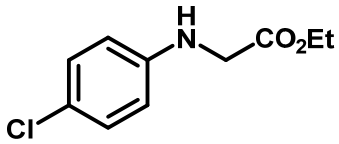
^{1}H NMR, **^{13}C NMR**: Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc*., 1996, **118**, 9901-9907.
MS (EI): A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



Diethyl 2,2'-(p-tolylazanediyl)diacetate was prepared from *p*-toluidine and EDA.

^{1}H NMR (δ, ppm): 1.30 (t, 6H, OCH_2CH_3), 2.27 (s, 3H, $CH_3C_6H_5$), 4.15 (s, 4H, NCH_2CH_3), 4.24 (q, 4H, OCH_2CH_3), 6.59 (d, 2H, C_6H_4), 7.07 (d, 2H, C_6H_4). **^{13}C NMR** (δ, ppm): 14.2, 54.0, 55.6, 60.9, 114.4, 114.7, 142.3, 152.6, 171.1. **MS (EI)** m/z (%): 279 (M^+,19), 207 (14), 206 (100), 134 (23), 120 (26), 119 (10), 118 (17), 105 (17), 91 (19), 59 (19).

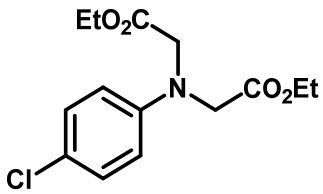
^{1}H NMR, **^{13}C NMR**: L. K. Baumann, H. M. Mbuvi, G. Du and L. K. Woo, *Organometallics*, 2007, **26**, 3995–4002.
MS (EI): A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



N-(4-chlorophenyl)glycine ethyl ester was prepared from 4-chloroaniline and EDA.

^{1}H NMR ($CDCl_3$), δ ppm 1.29 (t, 3H), 2.14 (s, 1H), 3.96 (s, 2H), 4.25 (q, 2H), 6.68-7.22 (m, 4H). **^{13}C NMR** ($CDCl_3$), δ ppm 14.21, 46.72, 60.31, 116.23, 129.51, 133.33, 145.01, 172.11. **MS (EI) m/z (%):** 213 (M^+, 18), 140 (100), 127 (1), 111 (11), 99 (1), 85 (1), 75 (10), 63 (1), 50 (3).

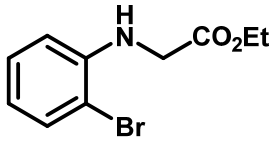
^{1}H NMR, **^{13}C NMR**: Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc*., 1996, **118**, 9901-9907.
MS (EI): A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



Ethyl N-ethoxycarbonylmethyl-N-(4-chlorophenyl)aminoacetate was prepared from 4-chloroaniline and EDA.

^{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). **MS (EI)** m/z (%): 299 (M^+, 17), 281 (2), 253 (1), 226 (100), 207 (4), 198 (4), 170 (3), 154 (15), 140 (36), 125 (21), 111 (14), 99 (2), 89 (3), 75 (8), 63 (1), 59 (45), 51(2).

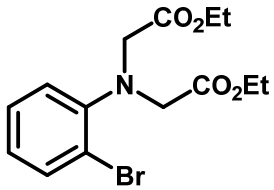
A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.*, 2023, **21**, 69–74.



Ethyl 2-((2-bromophenyl)amino)acetate was prepared from 2-bromoaniline and EDA.

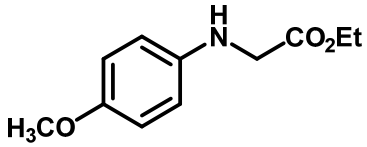
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 8.0, 1.6 Hz, 1H), 7.17 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 6.61 (td, J = 7.6, 1.6 Hz, 1H), 6.51 (dd, J = 8.0, 1.6 Hz, 1H), 4.97 (s, 1H), 4.26 (q, J = 7.2 Hz, 2H), 3.94 (d, J = 5.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 144.0, 132.6, 128.5, 118.6, 111.3, 110.0, 61.5, 45.7, 14.2. **MS (EI)** m/z (%): 259 (M^+, 16), 257 (M^+, 16), 186 (94), 184 (100), 104 (22), 77 (24).

^{1}H NMR, **^{13}C NMR**: J. Xie, Y. Huang, H. Song, Y. Liu and Q. Wang, *Org. Lett.* 2017, **19**, 6056–6059.



Diethyl 2,2'-((2-bromophenyl)azanediyl)diacetate was prepared from 2-bromoaniline and EDA.

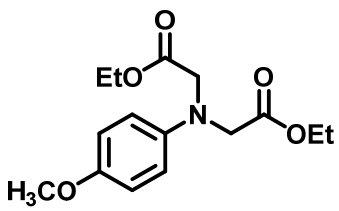
MS (EI) m/z (%): 345 (M^+, 8), 343 (M^+, 7), 272 (94), 270 (100), 200 (21), 186 (31), 169 (14), 104 (20), 91 (15), 77 (18), 59 (83).



Ethyl N-(4-methoxyphenyl)glycinate was prepared from *p*-methoxyaniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.79 (d, *J* = 8.9 Hz, 1H), 6.58 (d, *J* = 8.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 1H), 3.86 (s, 1H), 3.74 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (100 Hz, $CDCl_3$, 25 °C) δ: 14.4, 47.0, 55.9, 61.4, 114.6, 115.1, 141.5, 152.8,171.6. **MS (EI)** m/z (%): 209 (M^+, 24), 194 (1), 136 (100), 121 (10), 108 (6), 92 (7), 77 (6), 64 (3), 51 (1).

J. S. Samec, L. Mony and J.-E. Bäckvall, *Can. J. Chem.* 2005, **83,** 909-916.

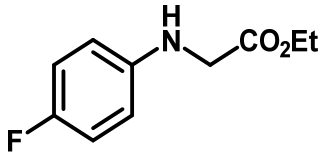


Diethyl 2,2'-((4-methoxyphenyl)azanediyl)diacetate was prepared from *p*-methoxyaniline and EDA.

^{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). **^{13}C NMR** (δ, ppm): 14.2, 54.0, 55.6, 60.9, 114.4, 114.7, 142.3, 152.6, 171.1. **MS (EI)** m/z (%): 295 (M^+, 25), 223 (14), 222 (100), 150 (21), 120 (25), 136 (19), 135 (19), 134 (10), 121 (11), 59 (18).

^{1}H NMR, **MS (EI)**: A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.

^{13}C NMR: L. K. Baumann, H. M. Mbuvi, G. Du and L. K. Woo, *Organometallics*, 2007, **26**, 3995–4002.

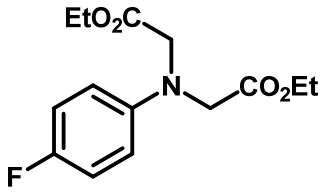


Ethyl 2-((4-Fluorophenyl)amino)acetate was prepared from *p*-fluoroaniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.95 – 6.85 (m, 2H), 6.59 – 6.48 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) (δ, ppm): 171.22, 157.90, 154.78, 143.53, 143.50, 116.05, 115.75, 114.05, 113.95, 61.50, 46.56, 14.32. **MS (EI)** m/z (%): 197 (M^+, 16), 124 (100), 111 (1), 95 (13), 83 (1), 75 (7), 69 (1), 50 (1).

^{1}H NMR, **MS (EI)**: A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.

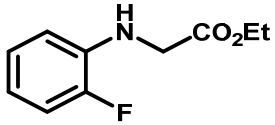
^{13}C NMR: R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño *J. Org. Chem.* 2013, **78,** 6050-6064.



Ethyl N-ethoxycarbonylmethyl-N-(4-fluorophenyl)aminoacetate was prepared from *p*-fluoroaniline and EDA.

^{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). **MS (EI)** m/z (%): 283 (M^+, 16), 211 (13), 210 (100), 138 (18), 124 (34), 123 (10), 122 (21), 109 (27), 95 (15), 59 (37).

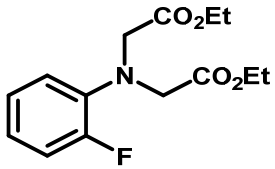
A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



Ethyl [(2-fluorophenyl)amino]acetate was prepared from 2-fluoroaniline and EDA.

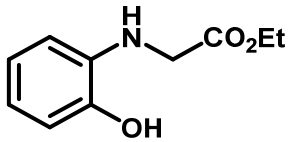
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.03 – 6.96 (m, 2H), 6.72 – 6.63 (m, 1H), 6.63 – 6.54 (m, 1H), 4.54 (bs, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.93 (d, *J* = 1.7 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 170.77 (s), 151.76 (d, *J* = 239.4 Hz), 135.72 (d, *J* = 11.7 Hz), 124.65 (d, *J* = 3.6 Hz), 117.72 (d, *J* = 7.0 Hz), 114.75 (d, *J* = 18.4 Hz), 112.34 (d, *J* = 3.1 Hz), 61.47 (s), 45.59 (s), 14.25 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) (δ, ppm): -135.86. **MS (EI) m/z (%):** 197 (M^+, 18), 124 (100), 111 (1), 102 (1), 95 (7), 83 (1), 77 (19), 75 (6), 69 (1), 63 (1), 57 (1), 51 (2).

L. P. Cailler, A. P. Kroitor, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Dalton Trans.* 2021, **50**, 2023–2031.



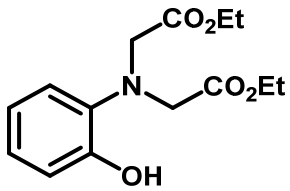
Diethyl 2,2'-((2-fluorophenyl)azanediyl)diacetate was prepared from 2-fluoroaniline and EDA.

^{1}H NMR (600 MHz, $CDCl_3$), δ 4.12 (d, 4H, (CH_2)-N), other signals were overlapped in the reaction mixture. **MS (EI)** m/z (%): 283(M^+, 15), 210 (100), 138 (33), 109 (29), 75 (8).



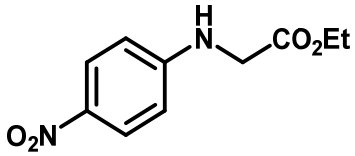
Ethyl (2-hydroxyphenyl)glycinate was prepared from 2-hydroxyaniline and EDA.
^{1}H NMR (DMSO-d_6, 300 MHz) 1.20 (t, 3H, J=7.2 Hz), 3.90 (d, 2H, J=6.0 Hz), 4.13 (q, 2H, J=7.2 Hz), 4.99 (t, 1H, J=6.0 Hz), 6.36 (dd, 1H, J=7.8 Hz, J=1.5 Hz), 6.46 (ddd, 1H, J=7.8 Hz, J=1.5 Hz), 6.61 (ddd, 1H, J=7.8 Hz, J=1.5 Hz), 6.68 (dd, 1H, J=7.8 Hz, J=1.5 Hz), 9.29 (s, 1H). **^{13}C NMR** (DMSO-d_6, 75 MHz) 14.02, 44.82, 60.26, 109.77, 113.49, 116.42, 119.52, 136.54, 144.06, 171.22. **MS (EI)** m/z (%): 195 (M^+, 33), 122 (100), 94 (14), 77 (13), 65 (9).

^{1}H NMR, **^{13}C NMR**: N. Zidar and D. Kikelj, *Tetrahedron* 2008, **64**, 5756–5761.



Diethyl 2,2'-((2-hydroxyphenyl)azanediyl)diacetate was prepared from 2-hydroxyaniline and EDA.

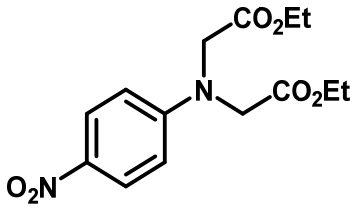
^{1}H NMR (600 MHz, $CDCl_3$), δ 4.06 (s, 4H, $(CH_2)_2$-N), other signals were overlapped in the reaction mixture. **MS (EI)** m/z (%): 281 (M^+, 1), 162 (94), 134 (100), 107 (13), 77 (27).



Ethyl (4-nitrophenyl)glycinate was prepared from 4-nitroaniline and EDA.

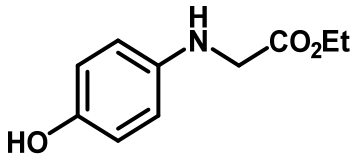
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, 3H, J = 7.1 Hz), 3.98 (s, 2H), 4.29 (q, 2H, J = 7.2 Hz), 5.12 (brs, 1H), 6.56 (d, 2H, J = 9.2 Hz), 8.12 (d, 2H, J = 9.2 Hz) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 14.2, 44.9, 62.0, 111.5, 126.4, 138.8, 151.9, 169.8 ppm. **MS (EI)** m/z (%): 224 (M^+, 17), 151 (100), 119 (9), 105 (38), 104 (9), 76 (7).

^{1}H NMR, **^{13}C NMR**: D. Kang, J. H. Ko, J. Choi, K. Cho, S. M. Lee, H. J. Kim, Y. J. Ko, K. H. Park and S. U. Son, *Chem. Commun.* 2017, **53**, 2598–2601.



Diethyl 2,2'-((4-nitrophenyl)azanediyl)diacetate was prepared from 4-nitroaniline and EDA.

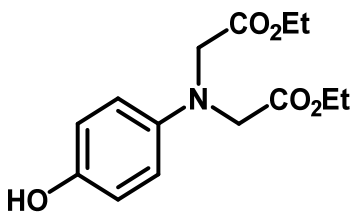
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.04 (s, 4H, $(CH_2)_2$-N), other signals were overlapped in the reaction mixture. **MS (EI)** m/z (%): 310 (M^+, 12), 237 (100), 151 (23), 105 (15), 77 (7).



Ethyl (4-hydroxyphenyl)glycinate was prepared from 4-hydroxyaniline and EDA.

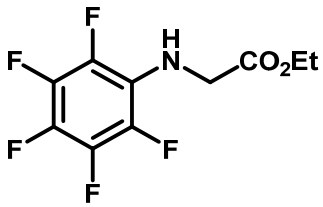
^{1}H NMR (600MHz, $CDC1_3$) δ 6.67 (d, J =7.1 Hz, 2H), 6.51 (d, J = 7 .1 Hz, 2H), 4.22 (dd, J = 14.0, 6.9 Hz, 2H), 3.83 (d, J = 17.3 Hz,2H), 1.30-1.25 (m, 3H). **^{13}C NMR** (151MHz, $CDCl_3$) 171.63 (d, J = 22.7 Hz), 148.64, 141.33 (d, J= 173.9 Hz), 116.19, 114.78, 61.33, 46.95, 15.92. **MS (EI)** m/z (%): 195 (M^+, 22), 122 (100), 94 (9), 65 (9).

^{1}H NMR, **^{13}C NMR**: Patent: Method for preparation of N-arylglycine ester derivatives, China, CN111333526 A 2020-06-26.



Diethyl 2,2'-((4-hydroxyphenyl)azanediyl)diacetate was prepared from 4-hydroxyaniline and EDA.

^{1}H NMR (600MHz, $CDC1_3$) δ 4.04 (s, 4H, $(CH_2)_2$-N), other signals were overlapped in the reaction mixture. **MS (EI)** m/z (%): 218(M^+, 67), 122 (63), 120 (100), 93 (27).



Ethyl [(2,3,4,5,6-pentafluorophenyl)amino]acetate was synthesized from 2,3,4,5,6-pentafluorofluoroaniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.24 (q, *J* = 7.1 Hz, 2H), 4.08 (dt, *J* = 6.2, 1.5 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 170.77, 139.71-139.15, 137.23-136.76, 135.50-135.14, 133.07-132.70, 123.31-123.02, 61.80, 47.33 (t, *J* = 4.2 Hz), 14.27. **^{19}F NMR** (376 MHz, $CDCl_3$) (δ, ppm): -159.50 – -159.74 (m), -163.99 – -164.28 (m), -170.64 (tt, *J* = 21.9, 6.1 Hz). **MS (EI)** m/z (%): 269 (M^+, 17), 196 (100), 177 (3), 167 (5), 149 (4), 137 (1), 126 (5), 117 (7), 106 (1) 99 (4), 93 (2), 75 (1), 69 (1).

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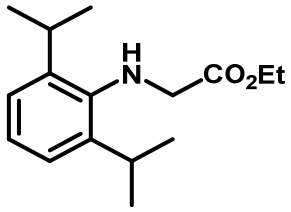

Ethyl [(2,6-diisopropylphenyl)amino]acetate was synthesized from 2,6-diisopropylaniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.14 – 7.04 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (bs, 1H), 3.74 (s, 2H), 3.32 (hept, *J* = 6.8 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 172.07, 142.85, 142.10, 123.98, 123.75, 61.31, 52.61, 27.95, 24.24, 14.31. **MS (EI)** m/z (%): 263 (M^+, 26), 248 (2), 234 (4), 220 (4), 190 (100), 176 (25), 160 (25), 146 (17), 132 (15), 117 (9), 103 (2), 91 (7), 77 (4), 65 (2), 51 (1).

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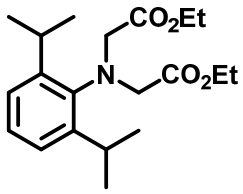

Diethyl 2,2'-((2,6-diisopropylphenyl)azanediyl)diacetate was synthesized from 2,6-diisopropylaniline and EDA.

^{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). **^{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. **MS (EI)** m/z (%): 349 (M^+, 6), 277 (19), 276 (100), 202 (11), 174 (7), 160 (6), 158 (7), 146 (10), 144 (7), 132 (14).

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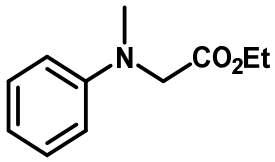
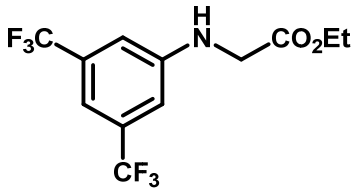


Ethyl (*N*-methyl-*N*-phenylamino)acetate was prepared from N-methylaniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.23 (t, *J* = 8.8 Hz, 2H), 6.74 (t, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 3.07 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (90.5 MHz, $CDCl_3$) 14.7, 39.9, 54.9, 61.2, 112.7, 117.7, 129.6, 149.4, 171.4. **MS (EI)** m/z (%): 193 (M^+, 13), 120 (100), 104 (10), 91 (4), 77 (13), 51 (4).

^{1}H NMR, ^{13}C NMR: S. L. Parisel, L. A. Adrio, A. Amoedo Pereira, M. Marino Pérez, J. M. Vila and K. K. Hii *Tetrahedron*, 2005, **61**, 9822-9826.

MS (EI): T. Satoh, A. Osawa, T. Ohbayashi and A. Kondo *Tetrahedron*, 2006, **62**, 7892-7901.



Ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate was prepared from 3,5-bis(trifluoromethyl)aniline and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.20 (s, 1H), 6.94 (s, 2H), 4.79 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.95 (d, *J* = 5.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 170.07 (s), 147.73 (s), 132.62 (q, *J* = 32.9 Hz), 123.58 (q, *J* = 272.7 Hz), 112.22 (d, *J* = 2.9 Hz), 111.58 – 110.01 (m), 61.93 (s), 45.31 (s), 14.21 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) (δ, ppm): -63.25. **MS (EI) m/z (%):** 315 (M^+, 18), 296 (14), 242 (100), 223 (5), 213 (11), 202 (1), 195 (11), 182 (1), 173 (4), 163 (6), 144 (6), 125 (3), 104 (1), 94 (1), 75 (3), 51 (1).

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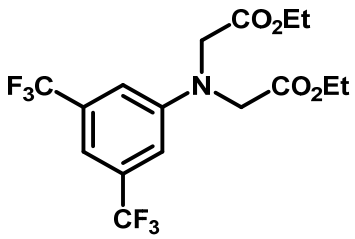
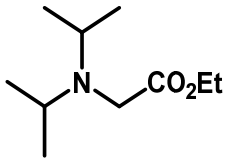


Diethyl 2,2'-((3,5-bis(trifluoromethyl)phenyl)azanediyl)diacetate was prepared from 3,5-bis(trifluoromethyl)aniline and EDA.

^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm): 4.07 (d, 4H, $(CH_2)_2$-N), other signals were overlapped in the reaction mixture. **MS (EI)** m/z (%): 401 (M^+, 10), 328 (100), 241 (42), 213 (12), 59 (86).

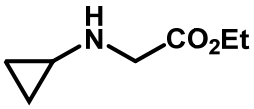


Ethyl diisopropylglycinate was prepared from diisopropylamine and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.14 (q, *J* = 7.1 Hz, 2H), 3.21 (s, 2H), 3.06 (hept, *J* = 6.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.1, 60.3, 50.0, 47.9, 20.5, 14.2 ppm. **MS (EI)** m/z (%): 187 (10), 172 (15), 144 (4), 130 (21), 114 (100), 102 (4), 84 (2), 72 (39), 56 (32).

^{1}H NMR, **^{13}C NMR**: L. Chen, H. Cui, Y. Wang, W. Liang, L. Zhang and C.-Y. Su, *Dalton Trans.*, 2018, **47**, 3940-3946.

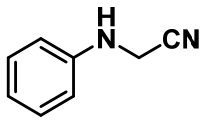
MS (EI): A. P. Kroitor, A. A. Dmitrienko, A. G. Martynov, Y. G. Gorbunova and A. B. Sorokin, *Org. Biomol. Chem.* 2023, **21**, 69–74.



Ethyl N-(cyclopropyl)glycinate was prepared from cyclopropylamine and EDA.

^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.19 (q, *J* = 7.1Hz 2H), 3.43 (s, 2H), 2.25 – 2.18 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.44 – 0.39 (m, 2H), 0.38 – 0.33 (m, 2H). **MS (EI)** m/z (%): 143 (M^+, 3), 114 (11), 97 (1), 86 (3), 70 (100), 56 (4).

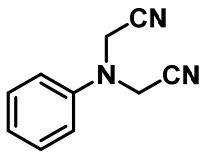
Y. Zhu, X. Zou, F. Hu, C. Yao, B. Liu and H. Yang, *J. Agric. Food Chem.* 2005, **53**, 9566-9570.



2-(phenylamino)acetonitrile was prepared from aniline and diazoacetonitrile.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98 (br. s, 1H), 4.08 (d, J = 7.1 Hz, 2H), 6.71 (d, J = 8.6 Hz, 2H), 6.89 (t, J = 8.5 Hz, 1H), 7.27 (t, J = 8.6 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, CDCl): δ 32.7, 113.6, 116.9, 120.1, 129.6, 145.0 ppm. **MS (EI)** m/z (%): 132 (M^+, 64), 104 (96), 92 (40), 77 (100), 51 (37).

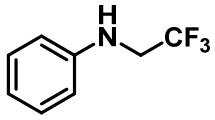
^{1}H NMR, **^{13}C NMR**: J. C. Castillo, J. Orrego-Hernández and J. Portilla, *European J. Org. Chem.*, 2016, **2016**, 3824–3835.



2,2'-(phenylazanediyl)diacetonitrile was prepared from aniline and diazoacetonitrile.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 (s, 3H), 7.00 (d, 2H, J = 7.5 Hz), 7.11 (t, 1H, J = 7.5 Hz), 7.39 (t, 1H, J = 7.5 Hz). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 41.0, 114.6, 117.2, 123.4, 130.0, 145.4. **MS(EI)** m/z (%): 171 (M^+, 100), 131 (80), 104 (61), 77 (78), 51 (24).

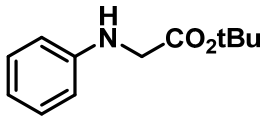
^{1}H NMR, **^{13}C NMR**: N. Sakai, N. Takahashi, D. Inoda, R. Ikeda and T. Konakahara, *Molecules*, 2013, **18**, 12488–12499.



N-(2,2,2-trifluoroethyl)aniline was prepared from aniline and 2,2,2-trifluorodiazoethane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.1 Hz, 2H), 6.88-6.72 (m, 3H), 3.94 (brs, 1H), 3.77 (q, J = 8.9 Hz, 2H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 146.26, 129.44, 126.47, 119.12, 113.14, 46.54. **MS(EI)** m/z (%): 175 (M^+, 59), 106 (100), 77 (29).

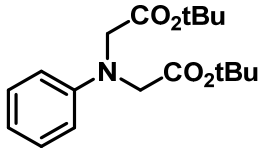
^{1}H NMR, **^{13}C NMR**: Y. Pan, Z. Luo, J. Han, X. Xu, C. Chen, H. Zhao, L. Xu, Q. Fan and J. Xiao, *Adv. Synth. Catal.*, 2019, **361**, 2301–2308.



***Tert*-butyl phenylglycinate** was prepared from aniline and *tert*-butyl diazoacetate.

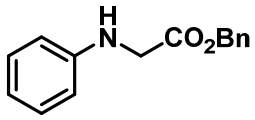
^{1}H NMR δ 1.48 (s, 9H), 3.79 (s, 2H), 4.24 (br, 1H), 6.60 (d, J = 7.6 Hz, 2H), 6.73 (t, J = 7.6 Hz, 1H), 7.18 (dd, J = 7.6, 7.6 Hz, 2H). **^{13}C NMR** δ 28.1, 46.5, 81.9, 113.0, 118.0, 129.2, 147.1, 170.2. **MS(EI)** m/z (%): 207 (M^+, 9), 106 (100), 77 (18), 51 (8).

^{1}H NMR, **^{13}C NMR**: G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2010, **132**, 10592–10608.



Di-*tert*-butyl 2,2'-(phenylazanediyl)diacetate was prepared from aniline and *tert*-butyl diazoacetate.

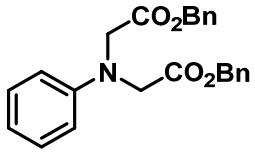
^{1}H NMR (400 MHz, $CDCl_3$) δ **^{1}H NMR** (600 MHz, $CDCl_3$) (δ, ppm): 4.00 (d, 4H, $(CH_2)_2$-N), other signals were overlapped in the reaction mixture. **MS (EI)** m/z (%): 321 (M^+, 8), 164 (100), 106 (28), 91 (24), 75 (17).



Benzyl phenylglycinate was prepared from aniline and benzyl diazoacetate.

^{1}H NMR δ 7.35 (5H), 7.18 (2H), 6.75 (1H), 6.60 (2H), 5.20 (2H), 3.94 (2H). **^{13}C NMR** δ 171.1, 147.0, 135.4, 129.4, 128.7, 128.6, 128.5, 118.4, 113.1, 67.1, 46.0. **MS (EI)**: 241 (M^+, 17), 106 (100), 91 (28), 77 (20).

^{1}H NMR, ^{13}C NMR: Y. Song, H. Zhang, J. Guo, Y. Shao, Y. Ding, L. Zhu and X. Yao, *European J. Org. Chem.*, 2021, **2021**, 5914–5921.



Dibenzyl 2,2'-(phenylazanediyl)diacetate was prepared from aniline and benzyl diazoacetate.

^{1}H NMR(400 MHz, $CDCl_3$) δ **^{1}H NMR** (600 MHz, $CDCl_3$) (δ, ppm): 4.19 (d, 4H, $(CH_2)_2$-N), other signals were overlapped in the reaction mixture. This product could not be analyzed by GC-MS because of its low volatility.