Supplementary Information

Selective carbene transfer to amines and olefins catalyzed by ruthenium phthalocyanine complexes with donor substituents

Lucie P. Cailler,[a] Andrey P. Kroitor,[b] Yulia G. Gorbunova,*[b,c] Alexander G. Martynov,*[b] Alexander B. Sorokin*[a]

[a] *Institut de Recherches sur la Catalyse et l'Environnement de Lyon IRCELYON, UMR 5256, CNRS - Université Lyon 1, 2 avenue A. Einstein, 69626 Villeurbanne cedex, France, e-mail: alexander.sorokin@ircelyon.univ-lyon1.fr*

[b] *A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr., 31, bldg. 4, 119071, Moscow, Russia, e-mail: martynov.alexandre@gmail.com*

[c] *N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr., 31, 11991, Moscow, Russia, e-mail: yulia@igic.ras.ru*

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1. Synthesis and characterization of ruthenium phthalocyanine complexes

Ruthenium(II) carbonyl complexes of octa-2,3,9,10,16,17,23,24-*n*-butoxyphthalocyanine [RuPc(OBu)$_8$](CO), tetra-2(3),9(10),16(17),23(24)-tert-butylphthalocyanine [RuPc(^{t}Bu$_4$)](CO) and octa-2,3,9,10,16,17,23,24-mesityloxyphthalocyanine [RuPc(OMes)$_8$](CO) were synthesized according to the previously reported procedures.[S1-S3]

Octa-2,3,9,10,16,17,23,24-n-butoxyphthalocyaninatoruthenium(II) carbonyl [RuPc(OBu)$_8$](CO)

- HR 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 2381.2 – $[M\text{-}CO]_2^+$, calculated for $[C_{128}H_{160}N_{16}O_{16}Ru_2]^+$ – 2381.0.
- UV-Vis in $CHCl_3$, λ_{max}, nm (lgε): 655 (5.09), 593 (4.43), 316 (4.92).
- ^{1}H NMR (400 MHz, $CDCl_3$+Py-d_5) δ 8.76 (s, 8H, H_{Pc}), 4.54 (br m, 16H, α-CH_2), 2.14 – 2.07 (m, 16H, β-CH_2), 1.78 – 1.69 (m, 16H, γ-CH_2), 1.13 (t, *J* = 7.4 Hz, 24H).
- ^{13}C NMR (101 MHz, $CDCl_3$+Py-d_5) δ 151.16 (a), 143.98 (d), 133.33 (c), 105.97 (b), 69.58 (α), 31.64 (β), 19.52 (γ), 14.10 ($\underline{C}H_3$).
- FTIR, ν cm^{-1}: 3848, 3731, 2956, 2930, 2870, 1939 (ν^{CO}), 1601, 1496, 1454, 1411, 1383, 1346, 1275, 1195, 1158, 1195, 1158, 1108, 1051, 953, 896, 856, 829, 859, 829, 750, 734, 667, 623, 608, 559, 551.

Tetra-2(3),9(10),16(17),23(24)-tert-butylphthalocyaninatoruthenium carbonyl [RuPc(^{t}Bu$_4$)](CO)

- HR ESI, m/z: found 865.3169 – $[M\text{-}H]^+$, calculated for $[C_{49}H_{48}N_8ORu\text{-}H]^+$ – 865.2924.
- MALDI TOF MS, m/z: found 1676.6 – $[M\text{-}CO]_2^+$, calculated for $[C_{96}H_{96}N_{16}Ru_2]^+$ –1676.6.
- UV-Vis in $CHCl_3$, λ_{max} nm (lgε): 653 (5.22), 591 (4.69), 298 (5.12).
- ^{1}H NMR (600 MHz, $CDCl_3$+Py-d_5) δ ppm: δ ppm 9.43 – 9.39 (m, 1H, $H_{Pc}2$), 9.32 – 9.25 (m, 1H, $H_{Pc}3$), 8.14 – 8.13 (m, 1H, $H_{Pc}1$), 1.78 – 1.77 (m, 9H, CH_3).
- FTIR, ν cm^{-1}: 2955, 2930, 2869, 1951 (ν^{CO}), 1606, 1495, 1453, 1407, 1379, 1346, 1275, 1197, 1155, 1108, 1049, 972, 939, 913, 893, 856, 820.

Octa-2,3,9,10,16,17,23,24-mesityloxyphthalocyaninatoruthenium(II) carbonyl [RuPc(OMes)$_8$](CO)

- HR ESI, m/z: found 1715.6353 – $[M]^+$, calculated for $[C_{105}H_{96}N_8O_9Ru]$ – 1715.6446.
- MALDI TOF MS, m/z: found 1686.7 – $[M\text{-}CO]^+$, calculated for $[C_{104}H_{96}N_8O_8Ru]^+$ – 1686.6; found 3375.4 – $[M\text{-}CO]_2^+$, calculated for $[C_{208}H_{192}N_{16}O_{16}Ru_2]^+$ – 3374.3.
- UV-Vis in $CHCl_3$, λ_{max} nm (lgε): 659 (5.00), 596 (4.32), 418 (3.98), 314 (4.81).

- ^{1}H NMR (600 MHz, $CDCl_3$+Py-d_5) δ 8.10 (s, 8H, H_{Ar}), 7.07 (s, 16H, $H_{Ar\text{-}Mes}$), 2.56 (s, 24H, *p*-CH_3), 2.36 (s, 48H, *o*-CH_3).
- FTIR, ν cm^{-1}: 2954, 2918, 2852, 1961(ν^{CO}), 1722, 1610, 1481, 1450, 1396, 1311, 1267, 1222, 1197, 1175, 1153, 1137, 1101, 1037, 955, 903, 880, 853, 752, 717, 592, 561, 553.

References

S1. A. Cidlina, J. Svec, L. Ludvová, J. Kuneš, P. Zimcik and V. Novakova, *J. Porphyrins Phthalocyanines* 2016, **20**, 1122–1133.
S2. A. P. Kroitor, L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze and A. B. Sorokin, *Dalton Trans.* 2017, **46**, 15651-15655.
S3. A. P. Kroitor, A. G. Martynov, Y. G. Gorbunova, A. Yu. Tsivadze and A. B. Sorokin, *Eur. J. Inorg. Chem*. 2019, 1923-1931.

2. Catalytic procedures

Cyclopropanation of olefins

All olefins were filtered through basic alumina and silica before use.

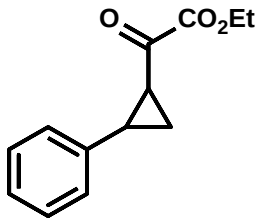
A 2 M solution of EDA in dichloromethane (0.23 mL, 0.48 mmol, 1.2 equiv.) was added to a solution of olefin (1 M, 0.4 mmol, 1 equiv.) and [RuPc(BuO)$_8$](CO) (1 mM, 4.10^{-4} mmol, 0.1 mol%) in 0.4 mL of dichloromethane under argon atmosphere via a syringe pump over 2h at 25°C. The reaction mixture was magnetically stirred for 2h to 2h30. Reaction products were analyzed by GC-MS and by NMR ($CDCl_3$) methods. Careful analyses of ^{1}H NMR and ^{19}F NMR (for fluorinated compounds) spectra with identification of all reaction products allowed for determination of conversion and product yields. The accuracy of this protocol was confirmed in separate experiments using 0.5 M CH_2Br_2 as internal standard. The products of several reactions were purified and isolated using PuriFlash XS 420 system (Interchim) at PF-15SIHP flash columns (cyclohexane/ethyl acetate). Analytical data for the reaction products were identical to those published in the literature.

Carbene N-H insertion of amines

EDA (91 µL, 0.5 mmol, 1 equiv.) was added to a solution of amine (1 M, 0.5 mmol, 1 equiv.) and [RuPc(BuO)$_8$](CO) (0.5 mM, 2.5.10^{-4} mmol, 0.05 mol%) in 0.5 mL of dichloromethane under argon atmosphere at 40°C. The reaction mixture was magnetically stirred for 10 min to 20 h at 40°C. Reaction products were analyzed by GC-MS and by ^{1}H NMR ($CDCl_3$) methods. Careful analyses of ^{1}H NMR and ^{19}F NMR (for fluorinated compounds) spectra with identification of all reaction products allowed for determination of conversion and product yields. The accuracy of this protocol was confirmed in separate experiments using 0.5 M CH_2Br_2 as internal standard. The products of several reactions were purified and isolated using PuriFlash XS 420 system (Interchim) at PF-15SIHP flash columns (cyclohexane/ethyl acetate). Analytical data for the reaction products were identical to those published in the literature.

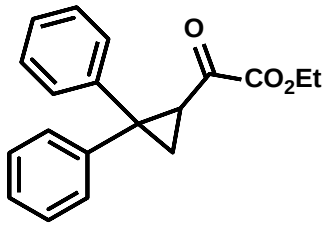
Nine novel compounds were additionally characterized by high resolution mass spectrometry (HRMS).

3. Characterization of products of cyclopropanation



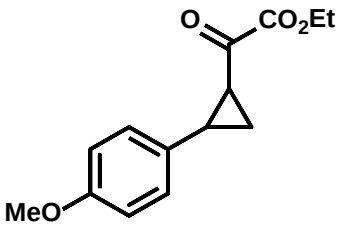
Ethyl 2-phenylcyclopropane-1-carboxylate was synthesized from styrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.04 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.54 (m, 1H), 1.91 (m, 1H), 1.61 (m, 1H), 1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 190 (M^+, 30), 144 (20), 117 (100), 91 (22).
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.25 - 7.18 (m, 5H), 3.87 (q, *J* = 7.1 Hz, 2H), 2.54 (m, 1H), 2.07 (m, 1H), 1.72 (m, 1H), 1.40 (m, 1H), 0.97 (3H, t, *J* = 7.1 Hz). **MS (EI) m/z (%):** 190 (M^+, 27), 144 (20), 117 (100), 91 (21).

H. Fritschi, U. Leutenegger and A. Pfaltz, *Helv. Chim. Acta*, 1988, **71**, 1553–1565.



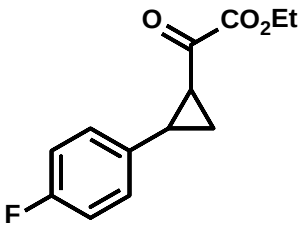
Ethyl 2,2-diphenylcyclopropane-1-carboxylate was synthesized from 1,1′-diphenylethylene and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.38–7.14 (m, 10H), 3.85–4.00 (m, 2H), 2.55 (dd, *J* = 6, 8 Hz, 1H), 2.17 (dd, *J* = 5 and 6 Hz, 1H), 1.59 (dd, *J* =5 and 8 Hz, 1H), 1.00 (t, *J* = 8 Hz, 3H). **MS (EI) *m/z* (%):** 237 [$(M - C_2H_5)^+$, 23] 192 (100), 165 (28), 115 (50), 91 (14).

C. J. Sanders, K. M. Gillespie and P. Scott, *Tetrahedron: Asymmetry*, 2001, **12**, 1055-1061.



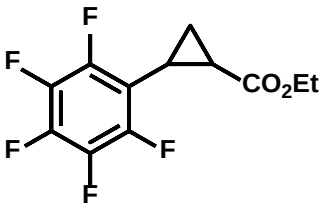
Ethyl 2-(4-methoxyphenyl)cyclopropane-1-carboxylate was synthesized from 4-methoxystyrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.04 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.48 (m, 1H), 1.82 (m, 1H), 1.55 (m, 1H), 1.30 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 220 (M^+, 37), 175 (21), 147 (100), 115 (20), 91 (21);
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): (δ, ppm) 7.18 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 2.03 (m, 1H), 2.52 (m, 1H), 1.30 (m, 1H), 1.65 (m, 1H), 1.02 (t, *J* = 7.1Hz, 3H). **MS (EI) m/z (%):** 220 (M^+, 34), 175 (17), 147 (100), 115 (20), 91 (22).

trans-isomer: T. Niimi, T. Uchida, R. Irie and T. Katsuki, *Adv. Synth. Catal.*, 2001, **343**, 79-88.
cis-isomer: T. Uchida, R. Irie and T. Katsuki , *Tetrahedron,* 2000, **56**, 3501-3509.



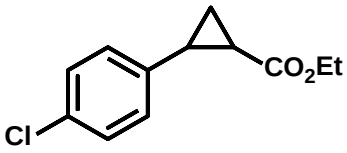
Ethyl 2-(4-fluorophenyl)cyclopropane-1-carboxylate was synthesized from 4-fluorostyrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.07 (d, 2H), 6.96 (d, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.50 (m, 1H), 1.84 (m, 1H), 1.58 (m, 1H), 1.33 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **MS (EI) *m/z* (%):** 208 (M^+, 32), 163 (27), 135 (100), 109 (24).
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.22 (d, 2H), 6.96 (d, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.53 (m, 1H), 2.12 (m, 1H), 1.67 (m, 1H), 1.25 (m, 1H), 1.01 (t, *J* = 7.2, 3H). **MS (EI) *m/z* (%):** 208 (M^+, 31), 163 (23), 135 (100), 109 (25).

trans-isomer: Y. Chen and X. P. Zhang, *J. Org. Chem.*, 2007, **72**, 5931-5934.
cis-isomer: A. Z. Kadzhaeva, E. V. Trofimova, A. N. Fedotov, K. A. Potekhin, R. A. Gazzaeva, S. S. Mochalov and N. S. Zefirov, *Chem. Heterocycl. Comp.*, 2009, **45**, 1095-1104.



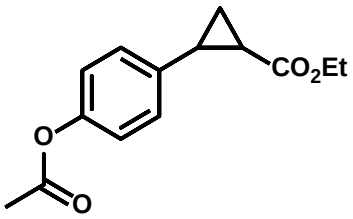
Ethyl 2-(pentafluorophenyl)cyclopropane-1-carboxylate was synthesized from 2,3,4,5,6-pentafluorostyrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 4.26 (q, *J* = 7.1 Hz, 2H), 2.45 (m, 1H), 2.15 (m, 1H), 1.63 (m, 1H), 1.50 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **MS (EI) *m/z* (%):** 280 (M^+, 52), 253 (39), 235 (62), 225 (30), 207 (68), 187 (100).
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 4.21 (q, *J* = 7.1 Hz, 2H), 2.45 (m, 1H), 2.15 (m, 1H), 1.63 (m, 1H), 1.54 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). **MS (EI) *m/z* (%):** 280 (M^+, 48), 253 (43), 235 (62), 225 (29), 207 (71), 187 (100).

trans-isomer: Y. Chen and X. P. Zhang , *J. Org. Chem.* 2007, **72**, 5931-5934.
cis-isomer: A. P. Kroitor, L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze and A. B. Sorokin, *Dalton Trans.* 2017, **46**, 15651-15655.



Ethyl 2-(4-Chlorophenyl)cyclopropane-1-carboxylate was synthesized from 4-chlorostyrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.24 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.48 (ddd, *J* = 9.4, 6.5, 4.2 Hz, 1H), 1.85 (ddd, *J* = 8.5, 5.3, 4.2 Hz, 1H), 1.63-1.55 (m, 1H), 1.37-1.21 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 224 (M+, 39), 196 (8), 178 (26), 169 (24), 161 (2), 151 (90), 144 (22), 138 (5), 132 (2), 125 (9), 115 (100), 103 (6), 97 (1), 89 (13), 75 (6), 63 (8), 51 (3), 39 (4).
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.31 (dd, *J* = 19.2, 8.6 Hz, 2H), 7.21 (d, *J* = 15.4, 8.6 Hz, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 2.51 (q, *J* = 8.6 Hz, 1H), 2.07 (ddd, *J* = 9.2, 7.9, 5.7 Hz, 1H), 1.69-1.63 (m, 1H), 1.37-1.21 (m, 1H), 1.02 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 224 (M+, 36), 196 (7), 178 (24), 169 (24), 161 (2), 151 (88), 144 (20), 138 (5), 132 (2), 125 (9), 115 (100), 103 (7), 89 (14), 77 (7), 63 (8), 51 (3), 39 (4).

trans-isomer: T. Niimi, T. Uchida, R. Irie and T. Katsuki, *Adv. Synth. Catal.* 2001, **1**, 79-88.
cis-isomer: T. Uchida, R. Irie, and T. Katsuki, *Tetrahedron* 2000, **56**, 3501-3509.

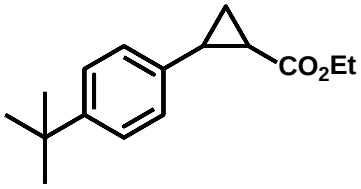


Ethyl 2-(4-acetoxyphenyl)cyclopropanecarboxylate was synthesized from 4-acetoxystyrene and EDA.

trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.10 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.48 (ddd, *J* = 9.4, 6.5, 4.2 Hz, 1H), 2.28 (s, 1H), 1.87 (ddd, *J* = 8.5, 5.3, 4.2 Hz, 1H), 1.62-1.54 (m, 1H), 1.37-1.21 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 248 (M+, 12), 206 (63), 193 (2), 177 (17), 160 (24), 149 (12), 133 (100), 123 (3), 115 (7), 105 (13), 91 (3), 77 (10), 65 (2), 55 (3), 43 (13).

cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.26 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 2.54 (q, *J* = 8.6 Hz, 1H), 2.27 (s, 1H), 2.07 (ddd, *J* = 9.2, 7.9, 5.7 Hz, 1H), 1.68 (dt, *J* = 7.4, 5.4 Hz, 1H), 1.37-1.21 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 248 (M+, 11), 206 (58), 193 (2), 177 (17), 160 (23), 149 (12), 133 (100), 123 (3), 115 (7), 105 (13), 91 (3), 77 (11), 65 (2), 55 (4), 43 (15).

L. Huang, Y. Chen, G.-Y. Gao and X. P. Zhang *J. Org. Chem.* 2003, **68**, 8179-8184.

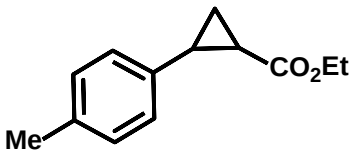


Ethyl 2-[4-(*tert*-butyl)phenyl]cyclopropane-1-carboxylate was synthesized from 4-*tert*-butylstyrene and EDA.

trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.30 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.48 (ddd, *J* = 9.4, 6.5, 4.2 Hz, 1H), 1.88 (ddd, *J* = 8.4, 5.3, 4.2 Hz, 1H), 1.60-1.53 (m, 1H), 1.40-1.20 (m, 1H), 1.30 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 246 (M+, 40), 231 (100), 217 (1), 203 (9), 191 (14), 173 (11), 161 (9), 157 (13), 144 (23), 128 (19), 115 (28), 105 (2), 91 (9), 79 (7), 71 (1), 64 (4), 57 (60), 41 (8).

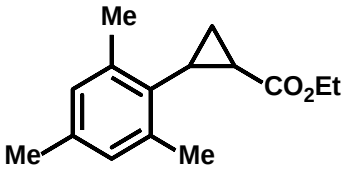
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 3.91-3.81 (m, 2H), 2.54 (dd, *J* = 7.6, 15.7 Hz, 1H), 2.04 (ddd, *J* = 9.3, 7.8, 5.7 Hz, 1H), 1.72-1.65 (m, 1H), 1.40-1.20 (m, 1H), 1.29 (s, 9H), 0.92 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 246 (M+, 36), 231 (100), 203 (8), 191 (4), 185 (8), 173 (11), 161 (10), 157 (13), 144 (25), 128 (21), 115 (33), 105 (3), 91 (11), 79 (8), 64 (5), 57 (71), 41 (10).

S. Bachmann and A. Mezzetti *Helv. Chim. Acta*, 2001, **84**, 3063-3074.



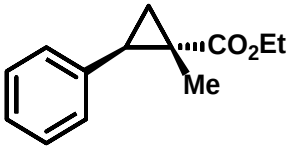
Ethyl 2-*p*-tolylcyclopropanecarboxylate was synthesized from 4-methylstyrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.08 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.51-2.45 (m, 1H), 2.31 (s, 3H), 1.85 (ddd, *J* = 8.5, 5.2, 4.2 Hz, 1H), 1.59-1.52 (m, 1H), 1.31-1.14 (m, 1H), 1.27 (t, *J* = 7 Hz, 3H). **MS (EI) m/z (%):** 204 (M+, 36), 175 (4), 158 (24), 147 (18), 141 (4), 131 (100), 121 (5), 115 (33), 103 (4), 91 (24), 77 (7), 65 (4), 51 (3), 39 (2).
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.15 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 2.56 (dd, *J* = 16.0, 7.8 Hz, 1H), 2.29 (s, 3H), 2.04 (ddd, *J* = 9.2, 7.8, 5.6 Hz, 1H), 1.69-1.63 (m, 1H), 1.32-1.27 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 204 (M+, 33), 175 (4), 158 (23), 147 (17), 141 (3), 131 (100), 121 (5), 115 (34), 103 (5), 91 (26), 77 (8), 65 (5), 51 (4), 39 (3).

trans-isomer: L. Huang, Y. Chen, G.-Y. Gao and X. P. Zhang *J. Org. Chem.* 2003, **68**, 8179-8184.
cis-isomer: M. Bordeaux, V. Tyagi and R. Fasan *Angew. Chem. Int. Ed.* 2015, **54**, 1744-1748.



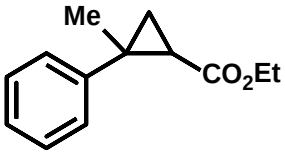
Ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate was synthesized from 2,4,6-trimethylstyrene and EDA.

trans-isomer: **HRMS (ESI+)** exact mass calculated for $[C_{15}H_{20}O_2 + Na]^+$: 255.1356, found : 255.1356. **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 6.83 (s, 2H), 4.31 – 4.14 (m, 2H), 2.34 (s, 6H), 2.30 (dd, *J* = 13.3, 8.2 Hz, 1H), 2.25 (s, 3H), 1.72 (dt, *J* = 8.3, 4.9 Hz, 1H), 1.69 – 1.62 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.13 (ddd, *J* = 8.2, 7.2, 4.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 174.49, 138.52, 136.51, 133.28, 129.04, 60.73, 23.32, 23.29, 20.94, 20.58, 17.73, 14.55. **MS (EI) m/z (%):** 232 (M+, 9), 217 (52), 203 (2), 187 (7), 175 (22), 159 (100), 143 (52), 129 (48), 115 (22), 105 (9), 91 (15), 77 (9), 65 (5), 51 (4).
cis-isomer: **HRMS (ESI+)** exact mass calculated for $[C_{15}H_{20}O_2 + Na]^+$: 255.1356, found : 255.1360. **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 6.78 (s, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 6H), 2.31 – 2.23 (m, 1H), 2.22 (s, 3H), 2.18 – 2.10 (m, 1H), 1.65 – 1.50 (m, 2H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 172.33, 138.28, 135.89, 130.67, 128.95, 60.23, 23.02, 21.21, 21.00, 20.64, 16.15, 14.09. **MS (EI) m/z (%):** 232 (M+, 51), 217 (2), 203 (8), 186 (19), 175 (22), 171 (12), 159 (100), 143 (54), 129 (46), 119 (19), 115 (23), 105 (9), 91 (16), 77 (10), 71 (3), 65 (5), 55 (4), 51 (4).



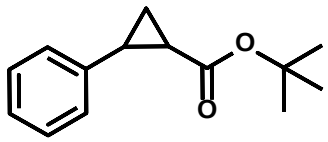
***Trans*-(1*R*,2*S*)-Ethyl 1-methyl-2-phenylcyclopropane-1-carboxylate** was synthesized from *trans*-β-methylstyrene and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34–7.18 (m, 3H), 7.11-7.04 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.40 (dd, *J* = 6.4, 5.1 Hz, 1H), 2.01 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.69 (dd, *J* = 12.6, 6.4 Hz, 1H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 204 (M+, 16), 189 (2), 175 (1), 159 (14), 144 (3), 131 (100), 115 (21), 103 (4), 91 (32), 77 (7), 65 (4), 58 (1), 51 (3), 39 (2).

T. Goto, K. Takeda, M. Anada, K. Ando and S. Hashimoto, *Tetrahedron Lett.* 2011, **52**, 4200-4203.



2-Methyl-2-phenyl-cyclopropanecarboxylic acid ethyl ester was synthesized from α-methylstyrene and EDA.
trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.24-7.12 (m, 5H), 4.19 (ddd, *J* = 14.2, 7.1, 2.4 Hz, 2H), 1.96 (dd, *J* = 8.3, 6.1 Hz, 1H), 1.52 (s, 3H), 1.43 (ddd, *J* = 12.9, 7.2, 4.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 204 (M+, 5), 189 (1), 175 (14), 159 (21), 147 (11), 141 (3), 131 (100), 121 (1), 115 (30), 103 (10), 91 (35), 77 (12), 65 (4), 58 (1), 51 (5), 43 (2).
cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.24-7.12 (m, 5H), 3.90-3.76 (m, 2H), 1.90 (dd, *J* = 7.8, 5.4 Hz, 1H), 1.77 (t, *J* = 5.0 Hz, 1H), 1.46 (s, 3H), 1.14 (dd, *J* = 7.8, 4.6 Hz, 1H), 0.94 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 204 (M+, 4), 189 (1), 175 (13), 159 (18), 147 (11), 141 (3), 131 (100), 121 (1), 115 (32), 103 (10), 91 (36), 77 (13), 65 (4), 58 (1), 51 (6), 43 (3).

K. C. Bendeddouche, B. Rechsteiner, F. Texier-Boullet, J. Hamelin and H. Benhaoua, *J. Chem. Res. (S)*, 2002, 114-117.



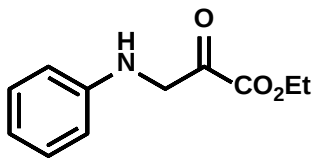
***tert*-Butyl 2-phenylcyclopropane-1-carboxylate** was synthesized from styrene and *tert*-butyl diazoacetate.

trans-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.29-7.08 (m, 5H), 2.64-2.58 (m, 1H), 2.05-1.98 (m, 1H), 1.72-1.64 (m, 1H), 1.41-1.34 (m, 1H), 1.35 (s, 9H). **MS (EI) m/z (%):** 218 (M^+, 0), 174 (6), 161 (1), 147 (1), 127 (2), 115 (15), 104 (6), 91 (100), 77 (3), 65 (6), 51 (2), 39 (2).

cis-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.29-7.16 (m, 5H), 2.64 (q, *J* = 9 Hz, 1H), 2.14-2.22 (m, 1H), 1.81-1.75 (m, 1H), 1.41-1.34 (m, 1H), 1.33 (s, 9H). **MS (EI) m/z (%):** 218 (M^+, 0), 174 (6), 161 (1), 147 (1), 127 (2), 115 (15), 104 (7), 91 (100), 77 (3), 65 (7), 51 (2), 39 (2).

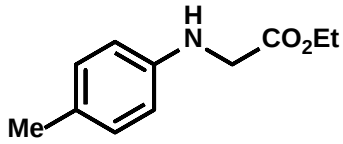
T. Niimi, T. Uchida, R. Irie and T. Katsuki *Adv. Synth. Catal.* 2001, **343**, 79-88.

4. Characterization of products of carbene insertion into N-H bonds



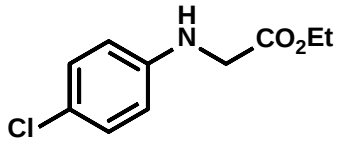
N-phenylglycine ethyl ester was synthesized from aniline and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.20 (t, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 179 (M^+, 19), 106 (100), 93 (1), 79 (6), 77 (22), 65 (1), 51 (8).

Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc*., 1996, **118**, 9901-9907.



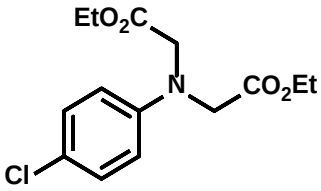
N-(4-methylphenyl)glycine ethyl ester was synthesized from *p*-toluidine and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.88 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 193 (M^+, 18), 120 (100), 104 (1), 91 (19), 89 (4), 77 (3), 65 (8), 63 (2), 51 (2).

Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc*., 1996, **118**, 9901-9907.



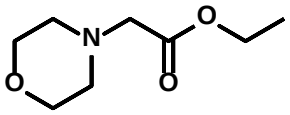
N-(4-chlorophenyl)glycine ethyl ester was synthesized from 4-chloroaniline and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.13 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 213 (M^+, 18), 140 (100), 127 (1), 111 (11), 99 (1), 85 (1), 75 (10), 63 (1), 50 (3).

Z. Zhu and J. H. Espenson, *J. Am. Chem. Soc*., 1996, **118**, 9901-9907.



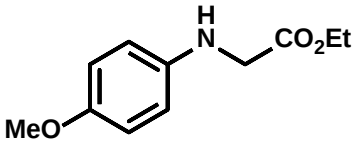
Ethyl N-ethoxycarbonylmethyl-N-(4-chlorophenyl)aminoacetate was synthesized from 4-chloroaniline and EDA.
MS (EI) m/z (%): 299 (M^+, 17), 281 (2), 253 (1), 226 (100), 207 (4), 198 (4), 170 (3), 154 (15), 140 (36), 125 (21), 111 (14), 99 (2), 89 (3), 75 (8), 63 (1), 59 (45), 51(2).

I. Aviv and Z. Gross, *Chem. Eur. J.* 2008, **14**, 3995-4005.



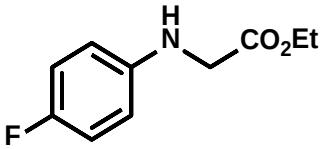
Ethyl 2-morpholinoacetate was synthesized from morpholine and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.17 (q, *J* = 7.1 Hz, 3H), 3.76 – 3.71 (m, 2H), 3.18 (s, 1H), 2.60 – 2.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 5H). **MS (EI) m/z (%):** 173 (M^+, 4), 114 (1), 100 (100), 70 (5), 56 (11).

I. Aviv and Z. Gross, *Chem. - Eur. J.*, 2008, **14**, 3995- 4005.



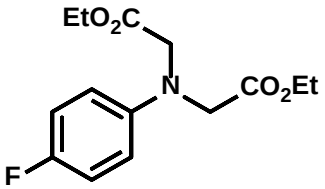
Ethyl N-(4-methoxyphenyl)glycinate was synthesized from *p*-methoxyaniline and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.79 (d, *J* = 8.9 Hz, 1H), 6.58 (d, *J* = 8.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 1H), 3.86 (s, 1H), 3.74 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 2H). **MS (EI) m/z (%):** 209 (M^+, 24), 194 (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.



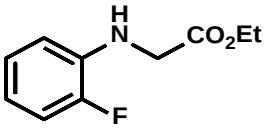
Ethyl 2-((4-Fluorophenyl)amino)acetate was synthesized from *p*-fluoroaniline and EDA. **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 6.95 – 6.85 (m, 2H), 6.59 – 6.48 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 197 (M^+, 16), 124 (100), 111 (1), 95 (13), 83 (1), 75 (7), 69 (1), 50 (1).

R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño *J. Org. Chem.* 2013, **78,** 6050-6064.

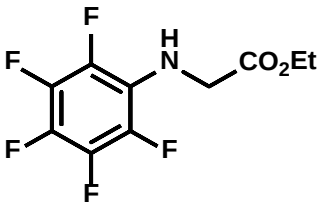


Ethyl N-ethoxycarbonylmethyl-N-(4-fluorophenyl)aminoacetate was synthesized from *p*-fluoroaniline and EDA.
MS (EI) m/z (%): 283 (M^+, 16), 237 (1), 210 (100), 182 (5), 154 (3), 138 (17), 124 (33), 109 (24), 95 (14), 75 (5), 59 (32).

Reference: Mitsubishi Pharma Corporation - US6455528, 2002, B1.



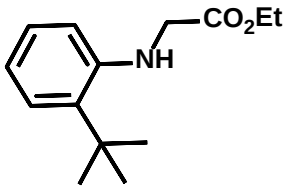
Ethyl [(2-fluorophenyl)amino]acetate was synthesized from 2-fluoroaniline and EDA.
HRMS (ESI+) exact mass calculated for $[C_{10}H_{12}FNO_2 + H]+$: 198.0925, found : 198.0929. **^{1}H NMR** (400 MHz, $CDCl_3$) (δ, ppm): 7.03 – 6.96 (m, 2H), 6.72 – 6.63 (m, 1H), 6.63 – 6.54 (m, 1H), 4.54 (bs, 1H), 4.25 (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).



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

HRMS (ESI+) exact mass calculated for $[C_{10}H_8F_5NO_2 + H]+$: 270.0548, found : 270.0549.

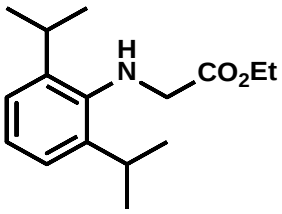
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.24 (q, *J* = 7.1 Hz, 2H), 4.08 (dt, *J* = 6.2, 1.5 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 170.77, 139.71-139.15, 137.23-136.76, 135.50-135.14, 133.07-132.70, 123.31-123.02, 61.80, 47.33 (t, *J* = 4.2 Hz), 14.27. **^{19}F 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).



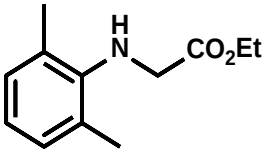
Ethyl [(2-*tert*-butylphenyl)amino]acetate was synthesized from 2-*tert*-butylaniline and EDA.

HRMS (ESI+) exact mass calculated for $[C_{14}H_{21}NO_2 + H]+$: 236.1645, found : 236.1648.

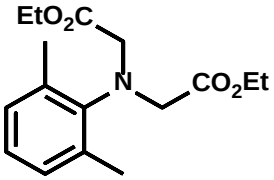
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.28 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.14 (td, *J* = 8.1, 1.4 Hz, 1H), 6.74 (td, *J* = 7.7, 1.3 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.74 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 4.8 Hz, 2H), 1.48 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 171.50, 145.25, 133.88, 127.31, 126.48, 117.71, 111.70, 61.55, 46.48, 34.28, 29.98, 14.33. **MS (EI) m/z (%):** 235 (M+, 29), 220 (8), 204 (2), 162 (100), 146 (29), 132 (26), 117 (14), 106 (11), 91 (12), 77 (8), 65 (3), 57 (2), 51 (2).



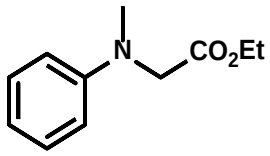
Ethyl [(2,6-diisopropylphenyl)amino]acetate was synthesized from 2,6-diisopropylaniline and EDA.
HRMS (ESI+) exact mass calculated for [$C_{16}H_{25}NO_2$ + H]+ : 264.1958, found : 264.1961.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.14 – 7.04 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (bs, 1H), 3.74 (s, 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).



Ethyl [(2,6-dimethylphenyl)amino]acetate was synthesized from 2,6-dimethylaniline and EDA.
HRMS (ESI+) exact mass calculated for [$C_{12}H_{17}NO_2$ + H]+ : 208.1332, found : 208.1331.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 6.99 (d, *J* = 7.5 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 1H), 3.82 (s, 2H), 2.33 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 172.39, 145.86, 128.99, 128.63, 121.90, 61.30, 50.15, 18.75, 14.28. **MS (EI) m/z (%):** 207 (M+, 41), 134 (100), 117 (11), 105 (25), 91 (8), 77 (17), 65 (5), 51 (3).

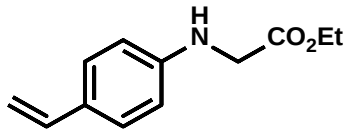


Ethyl N-ethoxycarbonylmethyl-N-(2,6-dimethylphenyl)aminoacetate was synthesized from 2,6-dimethylaniline and EDA.
HRMS (ESI+) exact mass calculated for [$C_{16}H_{23}NO_4$ + H]+ : 294.1700, found : 294.1709.
MS (EI) m/z (%): 293 (M+, 9), 264 (2), 247 (1), 220 (100), 206 (1), 192 (13), 164 (2), 146 (16), 132 (19), 117 (7), 105 (5), 91 (3), 77 (6), 65 (1), 59 (8), 51 (1).



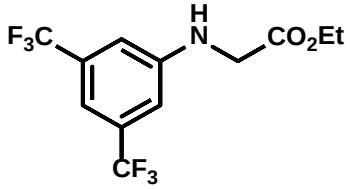
Ethyl (*N*-methyl-*N*-phenylamino)acetate was synthesized from N-methylaniline and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.23 (t, *J* = 8.8 Hz, 2H), 6.74 (t, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 3.07 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 193 (M+, 13), 120 (100), 104 (10), 91 (4), 77 (13), 51 (4).

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

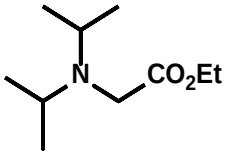


Ethyl [(4-ethenylphenyl)amino]acetate was synthesized from 4-aminostyrene and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.26 (d, *J* = 8.5 Hz, 2H), 6.61 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 2H), 5.54 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.03 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.90 (bs, 2H), 1.30 (t, *J* = 7.1 Hz, 1H). **MS (EI) m/z (%):** 205 (M+, 17), 132 (100), 103 (6), 77 (11).

Z. J. Wang, N. E. Peck, H. Renata and F. H. Arnold *Chem. Sci.*, 2014**, 5,** 598-601.

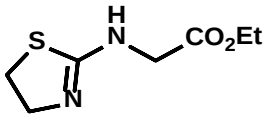


Ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate was synthesized from 3,5-bis(trifluoromethyl)aniline and EDA.
HRMS (ESI+) exact mass calculated for $[C_{12}H_{11}F_6NO_2 + H]^+$: 316.0767, found : 316.0768.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.20 (s, 1H), 6.94 (s, 2H), 4.79 (s, 1H), 4.28 (q, *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).



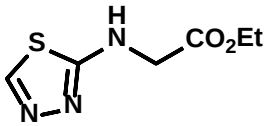
Ethyl diisopropylglycinate was synthesized from diisopropylamine and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.14 (q, *J* = 7.1 Hz, 2H), 3.21 (s, 2H), 3.06 (hept, *J* = 6.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 12H). **MS (EI) m/z (%):** 187 (10), 172 (15), 144 (4), 130 (21), 114 (100), 102 (4), 84 (2), 72 (39), 56 (32).

L. Chen, H. Cui, Y. Wang, W. Liang, L. Zhang and C.-Y. Su, *Dalton Trans.*, 2018, **47**, 3940-3946.



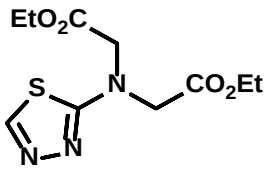
N-(4,5-dihydro-2-thiazolyl)glycine ethyl ester was synthesized from 2-aminothiazoline and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.11 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 188 (M+, 31), 170 (7), 142 (42), 129 (3), 115 (100), 101 (29), 88 (97), 86 (55), 72 (3), 56 (39).

L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze and A. B. Sorokin, *J. Porphyrins Phthalocyanines*, 2019, **23**, 497-506.



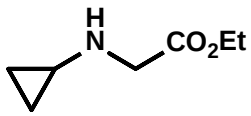
N-1,3,4-thiadiazol-2-ylglycine ethyl ester was synthesized from 2-amino-1,3,4-thiadiazole and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.47(s,1H), 5.54 (s, 2H), 4.25 (q,J= 7.1 Hz, 2H), 1.29 (t,J= 7.1 Hz, 3H). **MS (EI) m/z (%):** 187 (M+, 33), 169 (2), 142 (11), 114 (78), 101 (11), 88 (19), 74 (2), 60 (18), 55 (100).

N. E. A. Abdel-Sattar, A. M. El-Naggar and M. S. A. Abdel-Mottaleb *J. Chem.* 2017**,** 1-11.



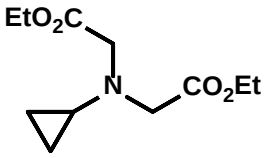
N-(2-ethoxy-2-oxoethyl)-N-1,3,4-thiadiazol-2-ylglycine ethyl ester was synthesized from 2-amino-1,3,4-thiadiazole and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.98 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.13 (t, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 3.55 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **MS (EI) m/z (%):** 273 (M+, 5), 228 (3), 200 (100), 172 (24), 126 (2), 114 (9), 100 (1), 72 (12), 55 (9).

L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze and A. B. Sorokin, *J. Porphyrins Phthalocyanines*, 2019, **23**, 497-506.

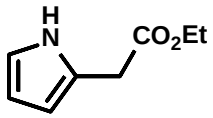


Ethyl N-(cyclopropyl)glycinate was synthesized from cyclopropylamine and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.19 (q, *J* = 7.1Hz 2H), 3.43 (s, 2H), 2.25 – 2.18 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.44 – 0.39 (m, 2H), 0.38 – 0.33 (m, 2H). **MS (EI) m/z (%):** 143 (M+, 3), 114 (11), 97 (1), 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.

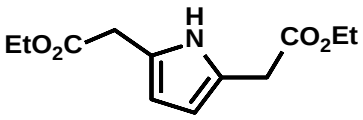


N-(2-ethoxy-2-oxoethyl)-N-(cyclopropyl)glycine ethyl ester was synthesized from cyclopropylamine and EDA.
HRMS (ESI+) exact mass calculated for $[C_{11}H_{19}NO_4 + H]+$: 230.1387, found : 230.1386.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 4.15 (q, *J* = 7.1 Hz, 13H), 3.65 (s, 12H), 2.48 (tt, *J* = 6.4, 3.8 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 20H), 0.53 – 0.42 (m, 13H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 171.56, 60.50, 55.02, 35.90, 14.36, 7.73. **MS (EI) m/z (%):** 229 (M+, 12), 200 (15), 172 (3), 156 (100), 142 (4), 128 (13), 114 (10), 110 (2), 100 (4), 84 (16), 82 (10), 70 (6), 68 (9), 59 (14), 55 (5).



Ethyl 2-(2-pyrrolyl)acetate was synthesized from pyrrole and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.73 (br s, 1H, NH), 6.75 (dd, *J* = 2.9, 4.2 Hz, 1H), 6.14 (dd, *J* = 2.5, 2.9 Hz, 1H), 6.04-5.99 (br m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 171.36, 123.47, 117.82, 108.40, 107.40, 61.73, 33.36, 14.31. **MS (EI) m/z (%):** 153 (M+, 25), 106 (1), 80 (100), 53 (11).

J.S. Yadav, B.V.S. Reddy and G. Satheesh *Tetrahedron Lett.,* 2003, **44**, 8331-8334.



Diethyl pyrrole-2,5-diacetate was synthesized from pyrrole and EDA.
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 9.02 (bs, 1H, NH), 5.91 (d, *J* = 2.5 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.62 (s, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) (δ, ppm): 171.13, 123.50, 107.44, 61.16, 33.56, 14.26. **MS (EI) m/z (%):** 239 (M+, 23), 166 (100), 138 (7), 120 (27), 93 (28), 65 (7), 52 (3).

R. Li, D. S. Larsen and S. Brooker *New J. Chem.,* 2003, **27**, 1353-1359.

5. NMR analysis of typical reaction mixtures after reaction completion

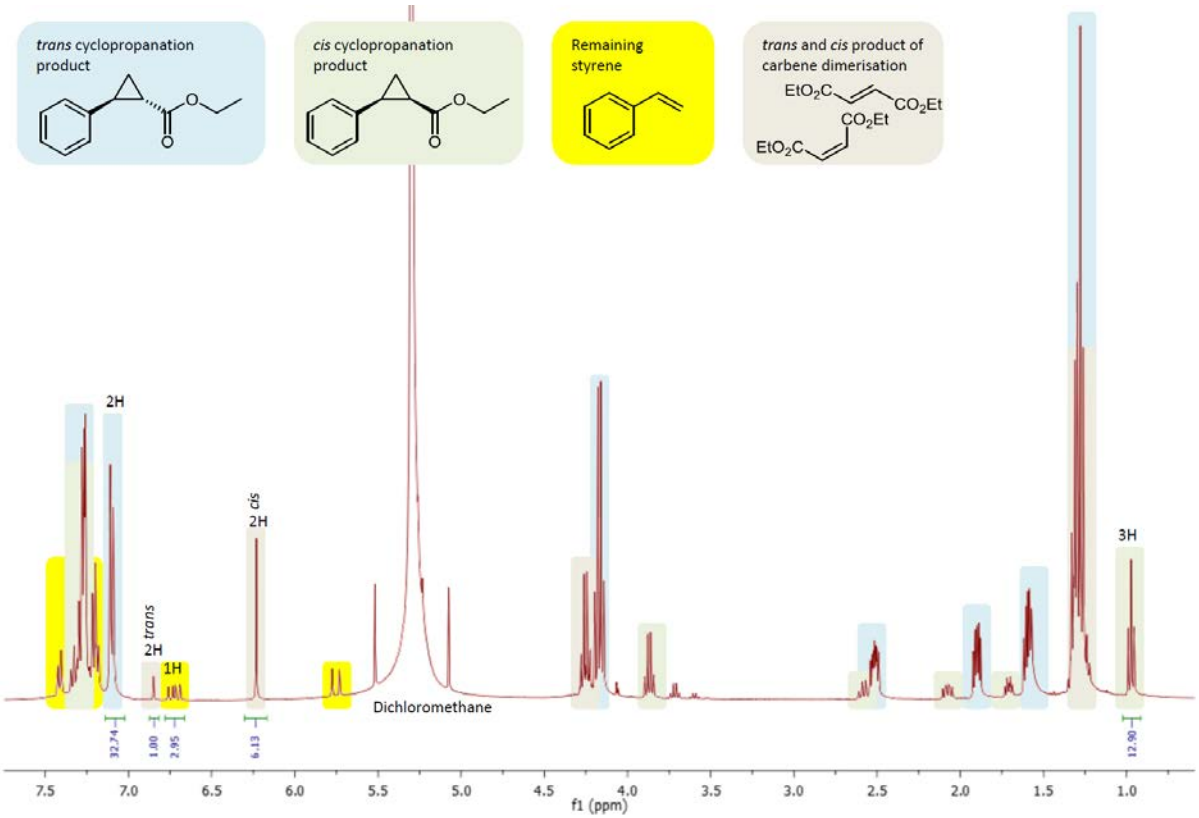


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the reaction mixture after completion of the reaction between styrene and EDA (Table 2, entry 1).

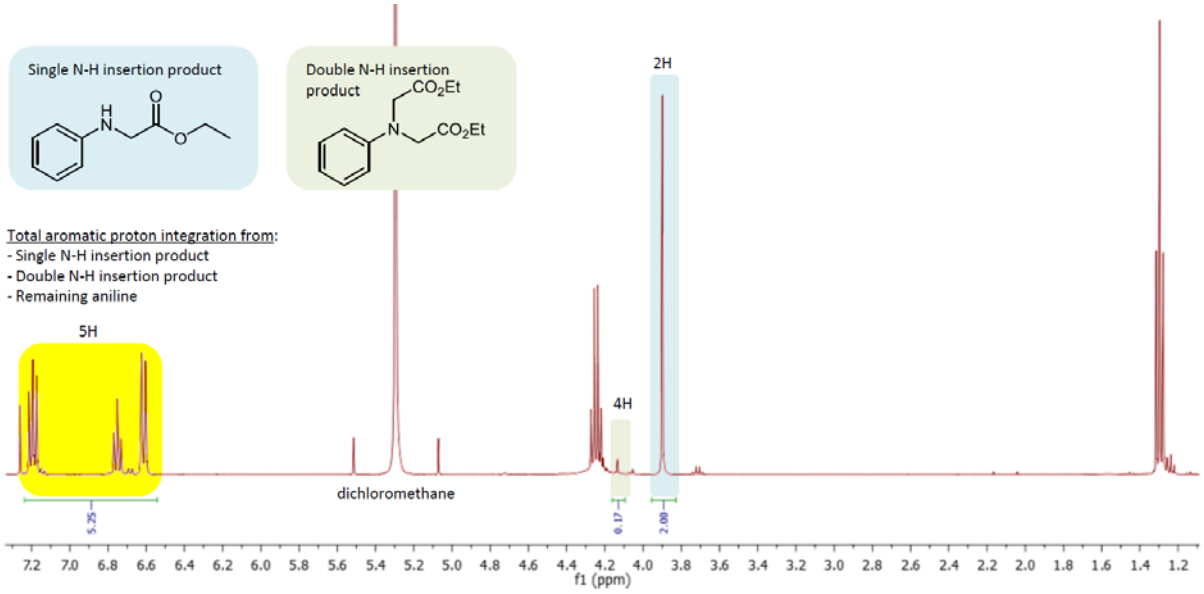


Figure S2: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the reaction mixture after completion of the reaction between aniline and EDA (Table 6, entry 1).

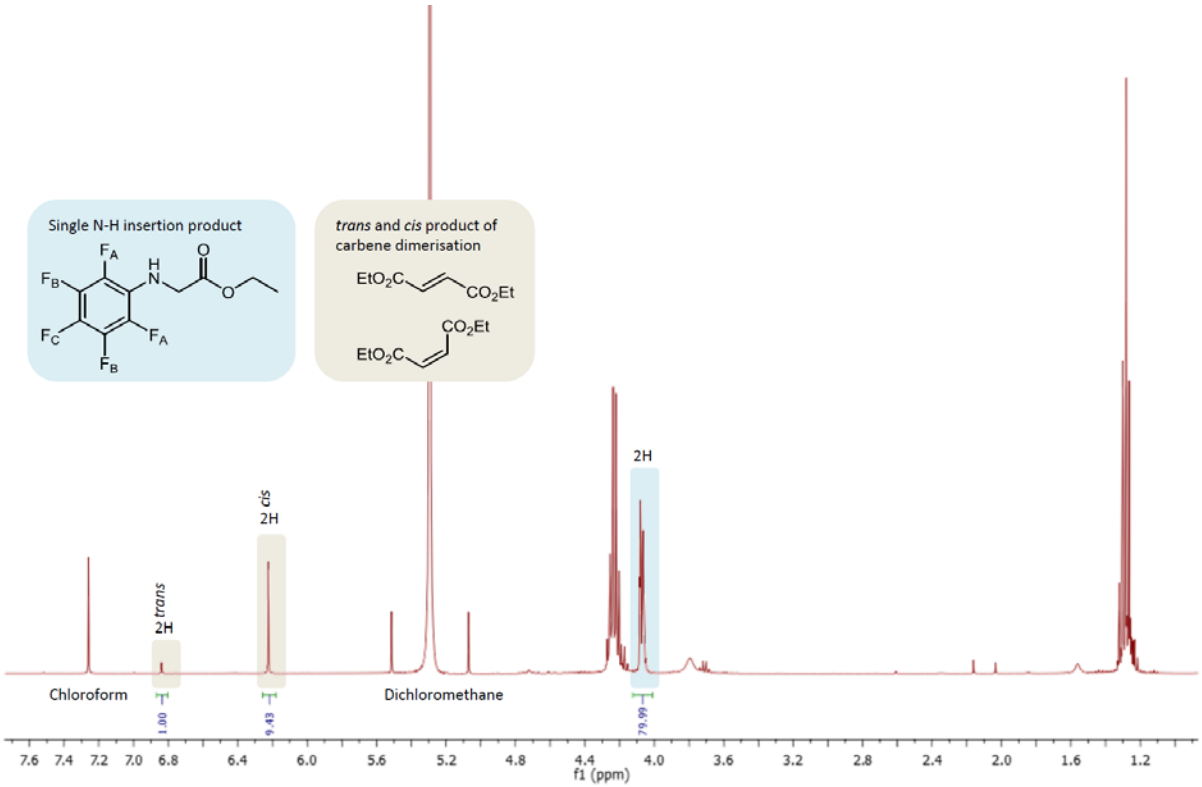


Figure S3: ^{1}H NMR spectrum ($CDCl_3$, 101 MHz) of the reaction mixture after completion of the reaction between 2,3,4,5,6-pentafluoroaniline and EDA (Table 6, entry 8).

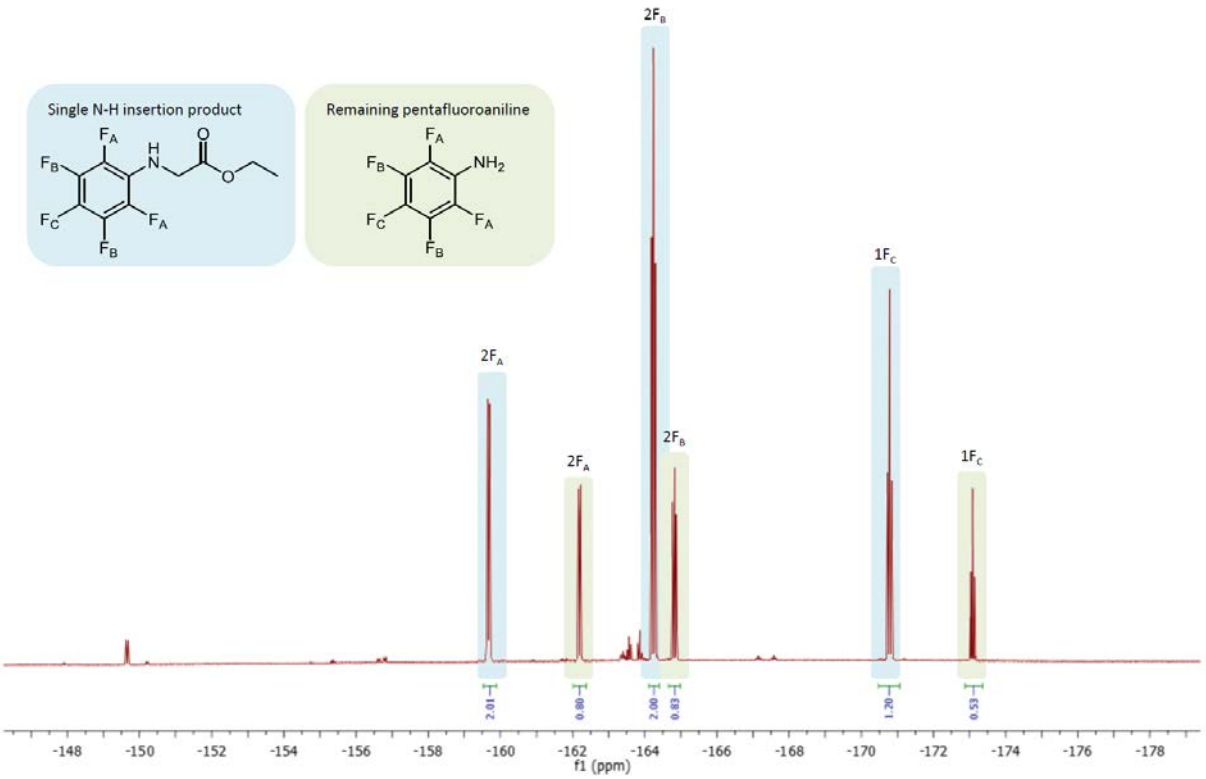
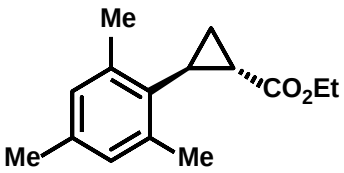


Figure S4: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of the reaction mixture after completion of the reaction between aniline and EDA (Table 6, entry 8).

6. Spectral data of new compounds (HRMS, ^{1}H, ^{13}C, ^{19}F NMR, Mass)



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

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Acquisition Parameter

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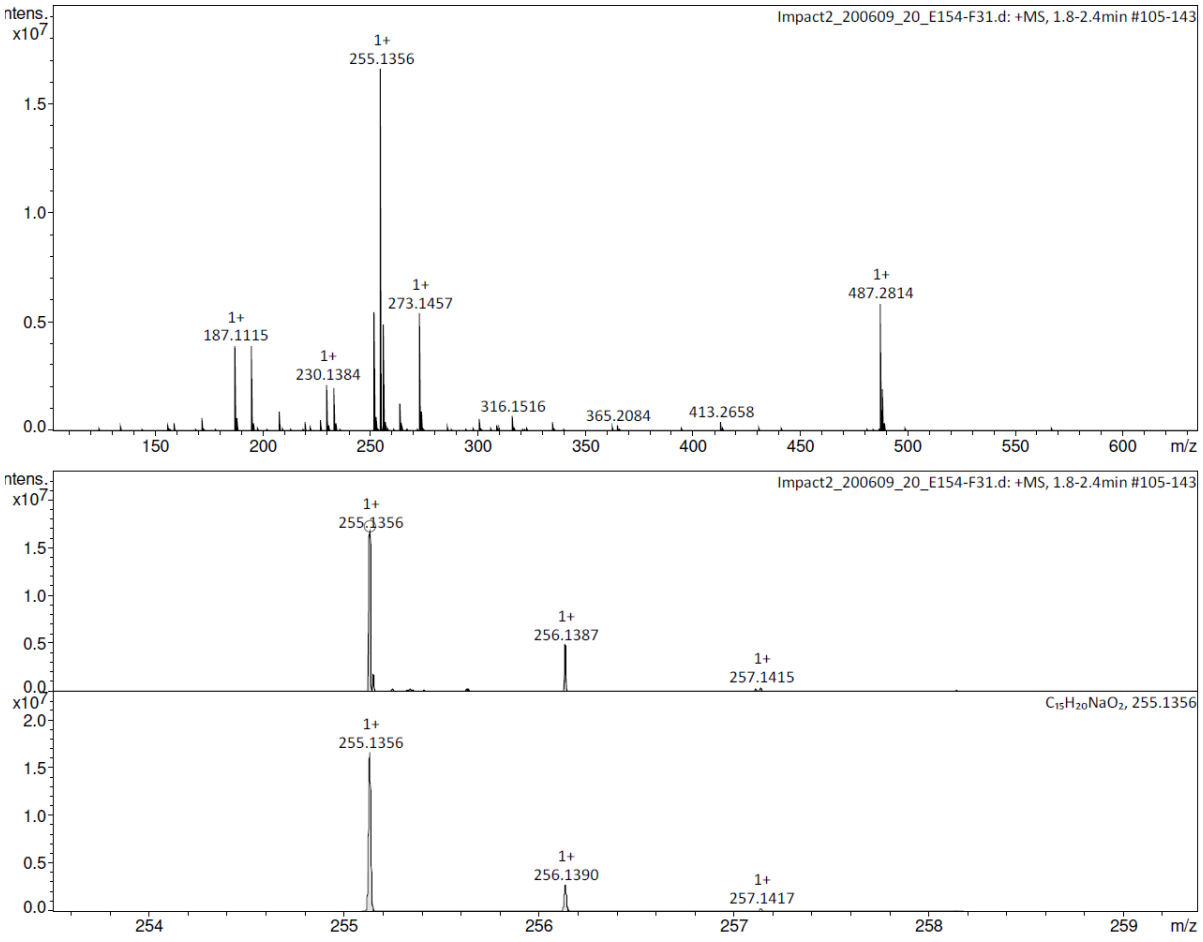
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
255.1356	C15H20NaO2	255.1356	C15H20O2	-0.2	74.7	M+Na	1+
487.2814	C30H40NaO4	487.2819		1.0	4.0	2M+Na	1+

Bruker Compass DataAnalysis 4.4 Page 1 of 1

Figure S5: HRMS spectrum of *trans*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).

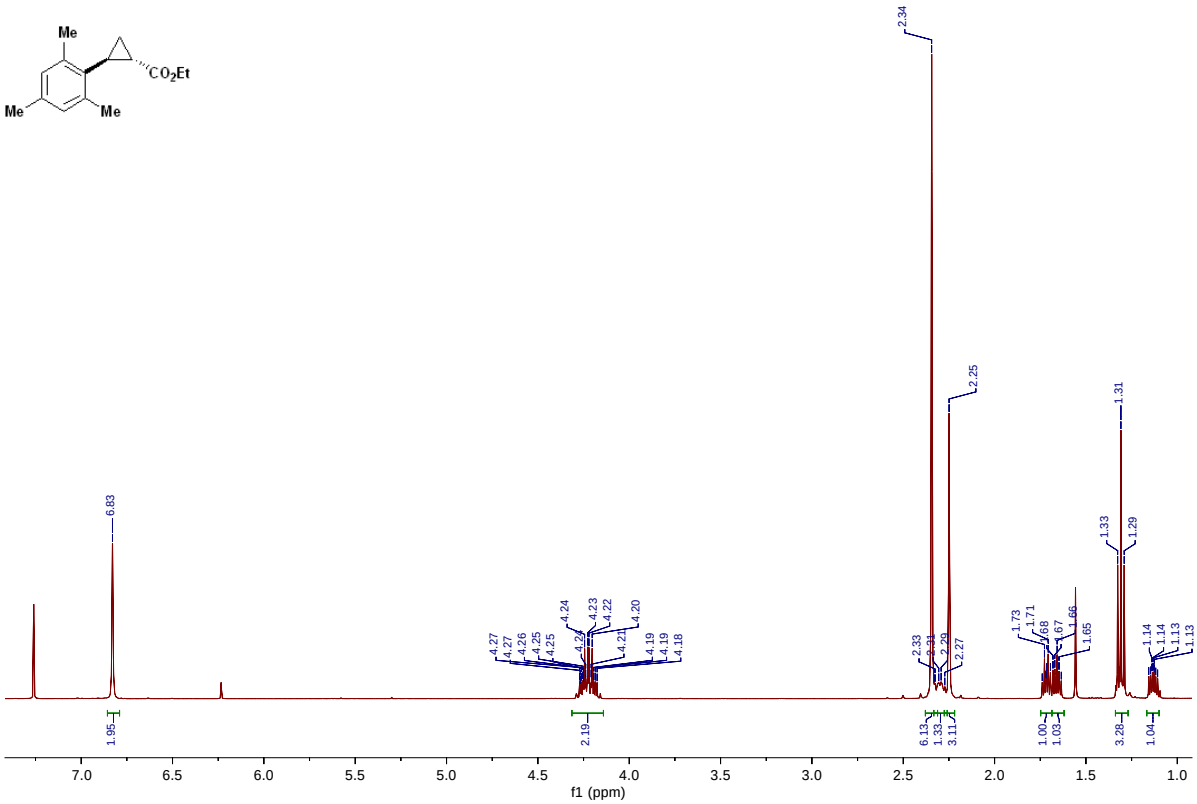


Figure S6: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *trans*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).

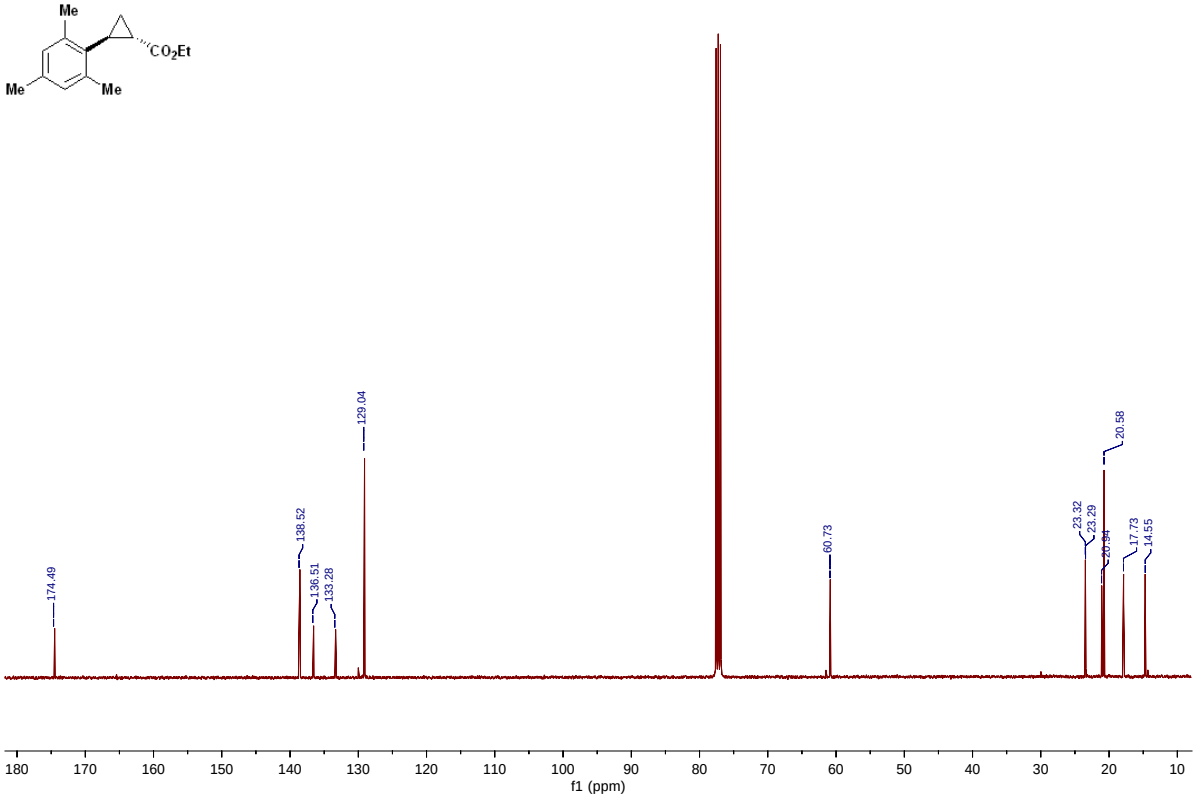


Figure S7: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of *trans*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).

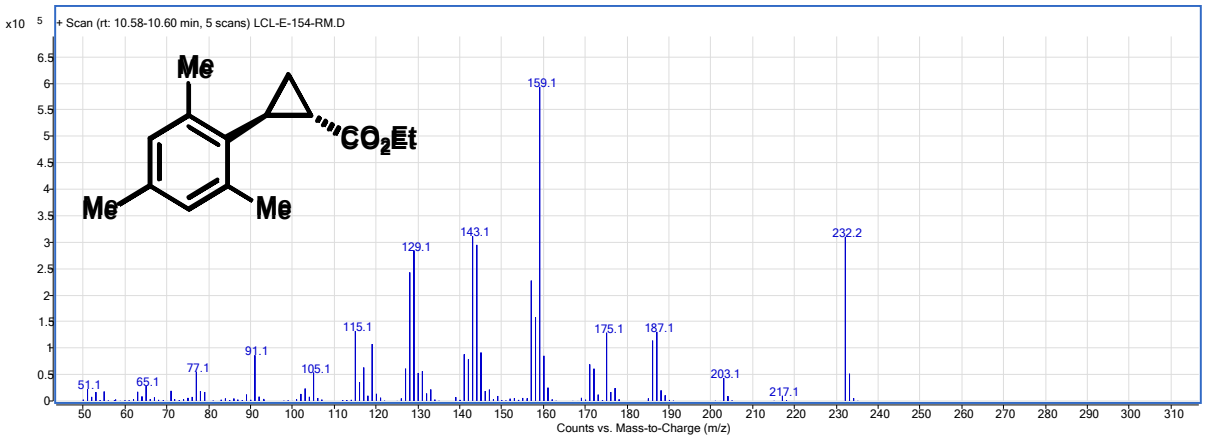
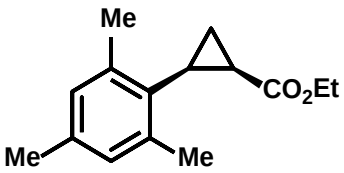


Figure S8: Mass spectrum (EI) of *trans*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

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Acquisition Parameter

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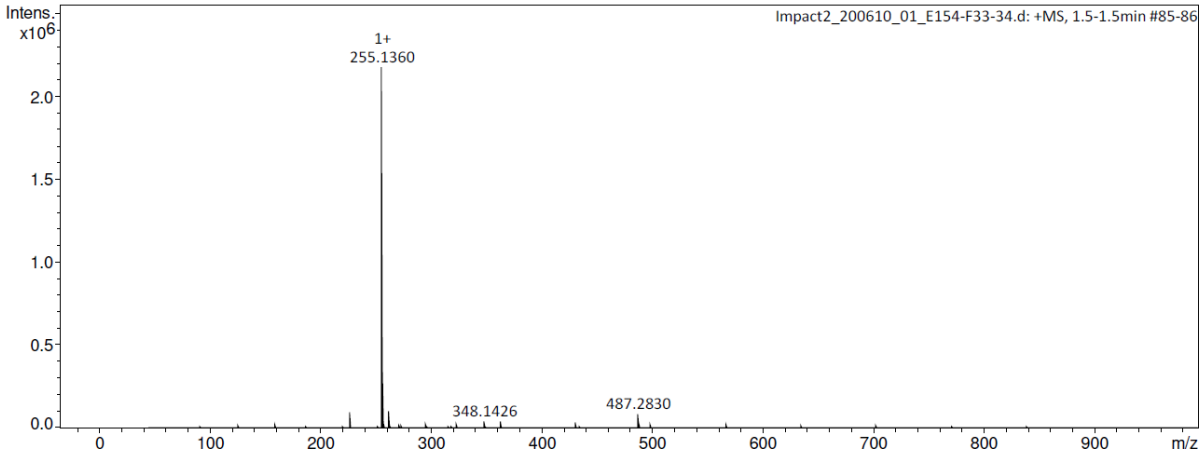
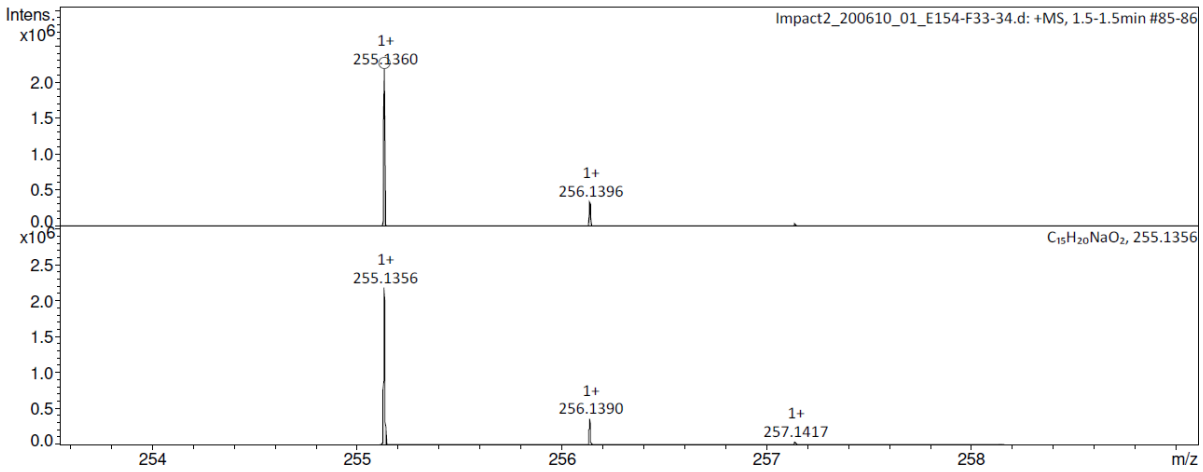
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
255.1360	C15H20NaO2	255.1356	C15H20O2	-1.7	6.9	M+Na	1+
487.2830	C30H40NaO4	487.2819		-2.2	17.8	2M+Na	1+

Bruker Compass DataAnalysis 4.4 Page 1 of 1

Figure S9: HRMS spectrum of *cis*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).

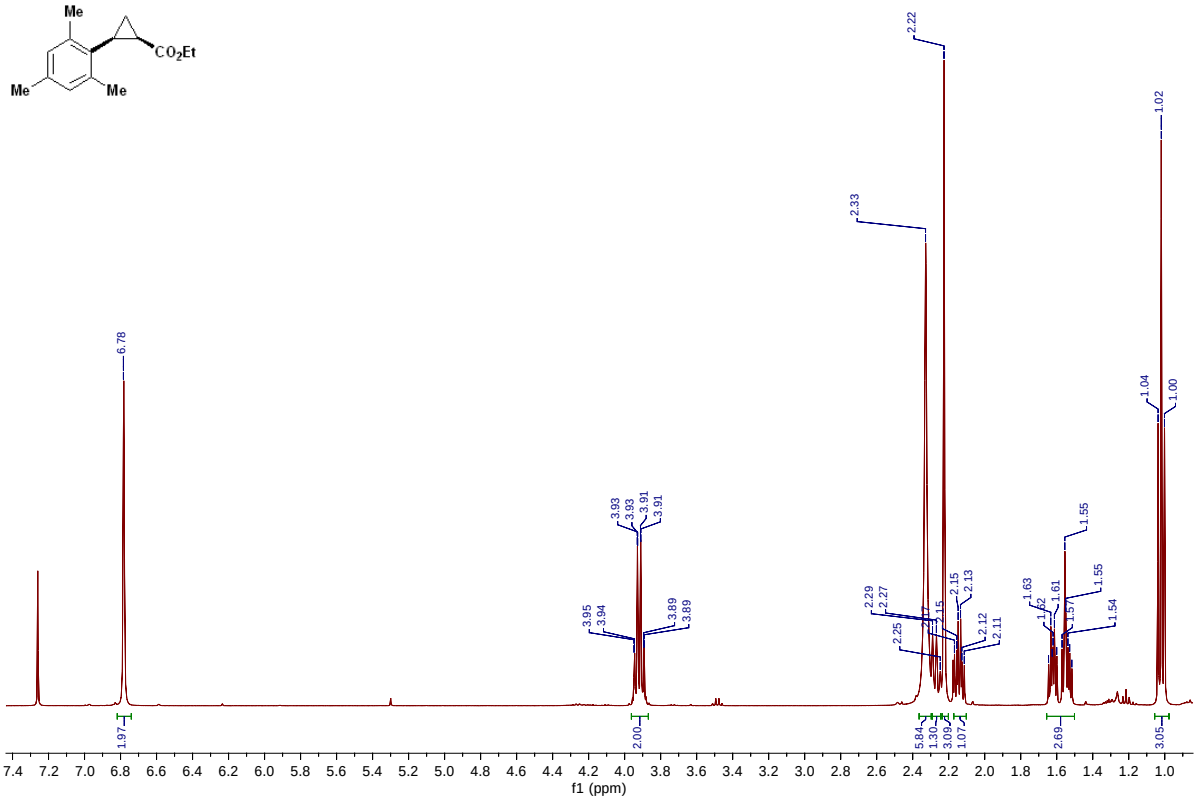


Figure S10: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of *cis*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).

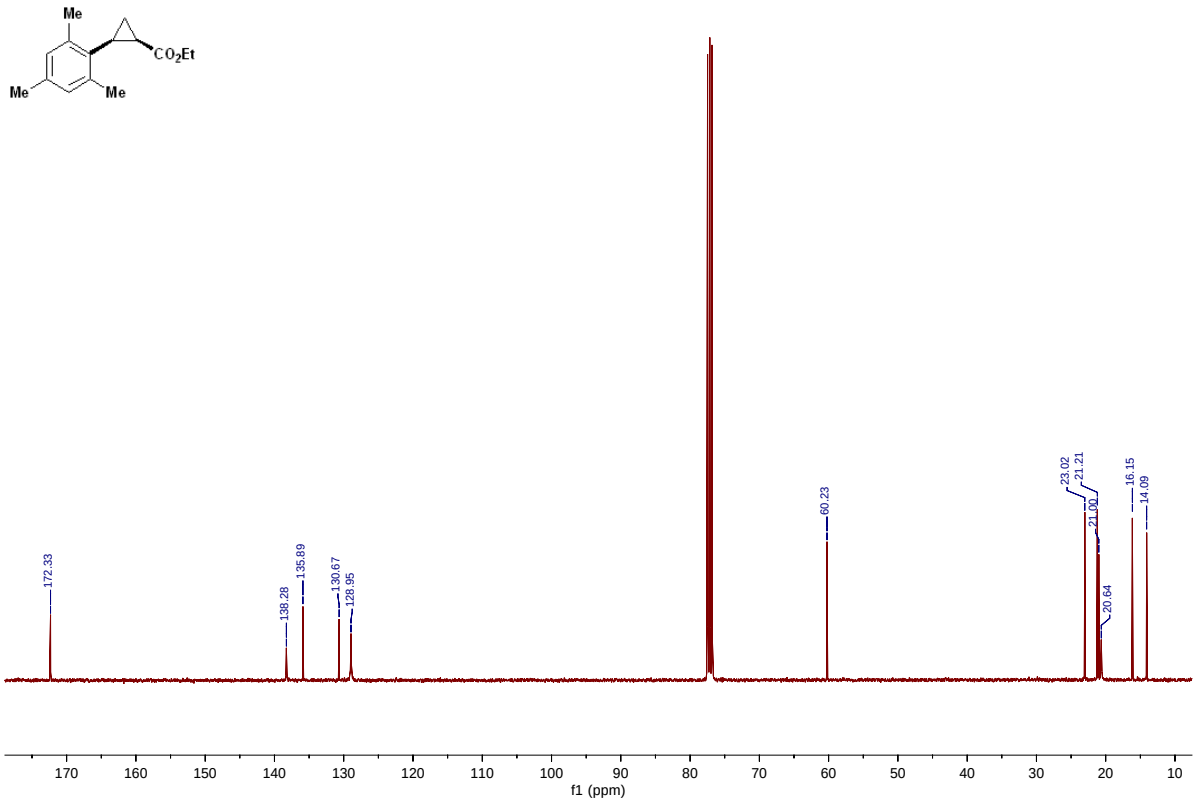


Figure S11: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of *cis*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).

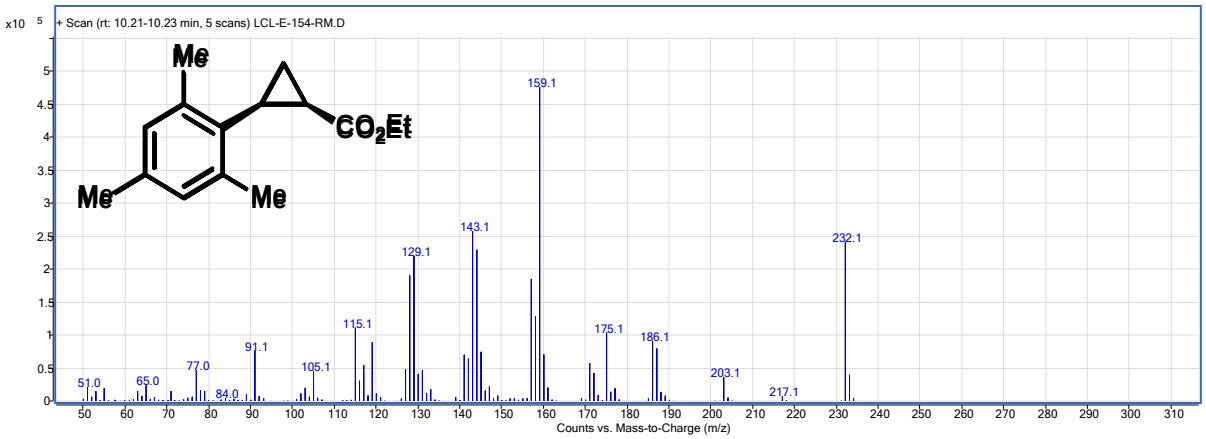
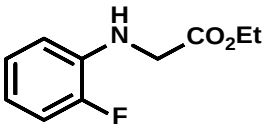


Figure S12: Mass spectrum (EI) of *cis*-ethyl 2-[2,4,6-trimethylphenyl]cyclopropane-1-carboxylate isolated by column chromatography from reaction between 2,4,6-trimethylstyrene and EDA (Table 2, entry 10).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

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Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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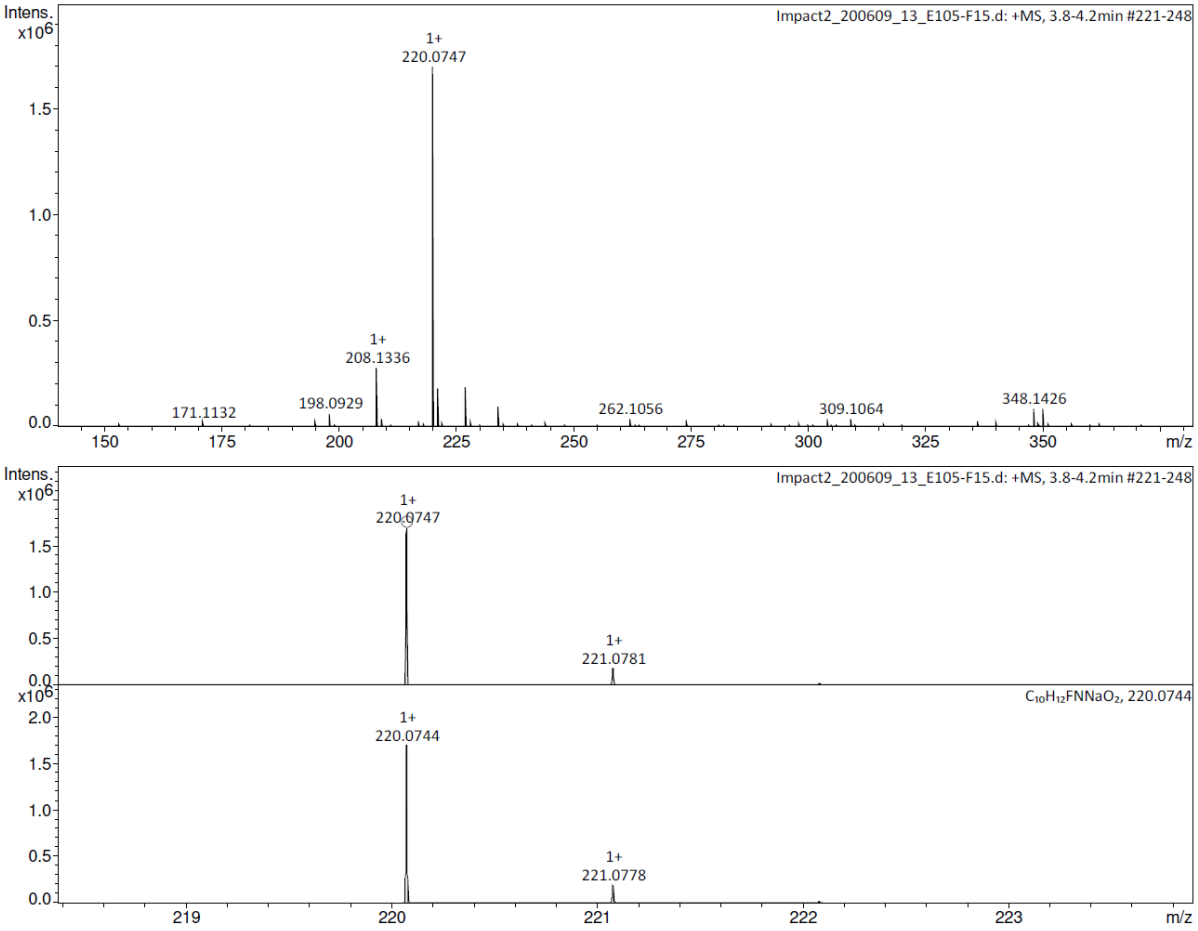
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
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220.0747	C10H12FNNaO2	220.0744		-1.3	4.8	M+Na	1+

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Figure S13: HRMS spectrum of ethyl [(2-fluorophenyl)amino]acetate isolated by column chromatography from reaction between 2-fluoroaniline and EDA (Table 6, entry 6).

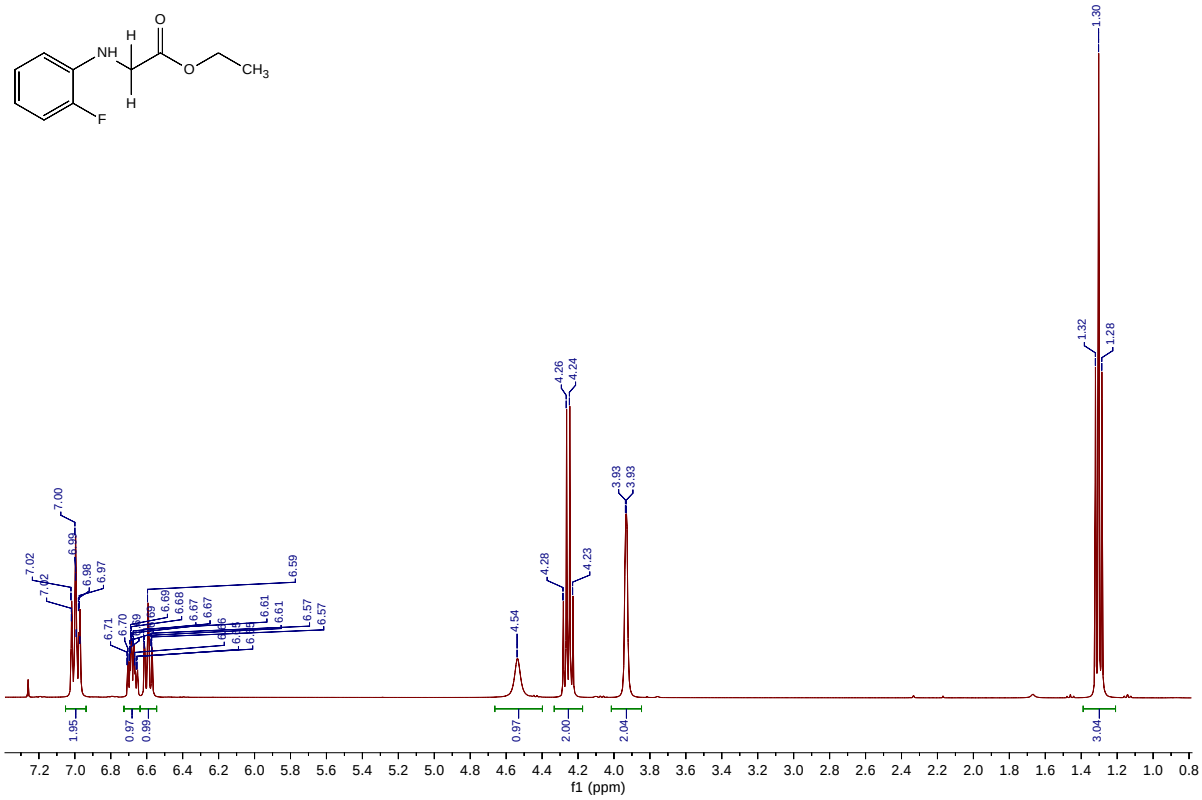


Figure S14: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl [(2-fluorophenyl)amino]acetate isolated by column chromatography from reaction between 2-fluoroaniline and EDA (Table 6, entry 6).

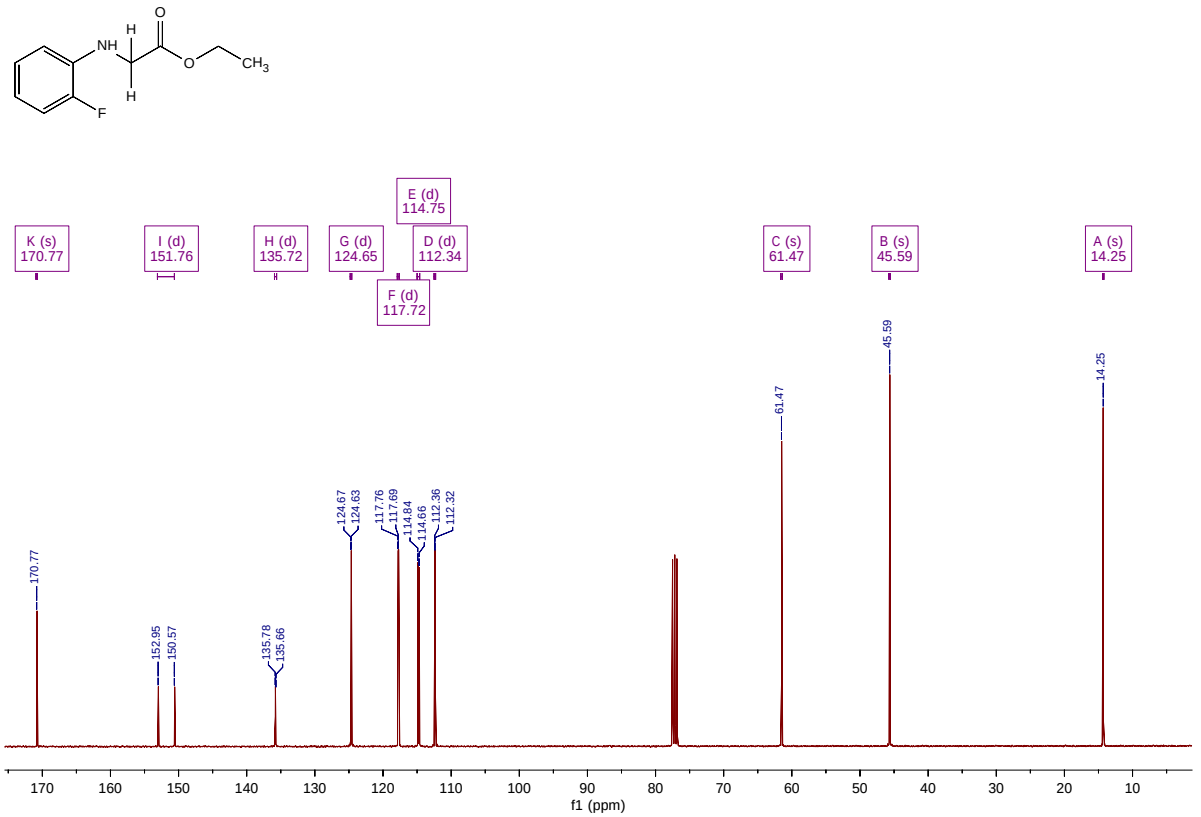


Figure S15: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of ethyl [(2-fluorophenyl)amino]acetate isolated by column chromatography from reaction between 2-fluoroaniline and EDA (Table 6, entry 6).

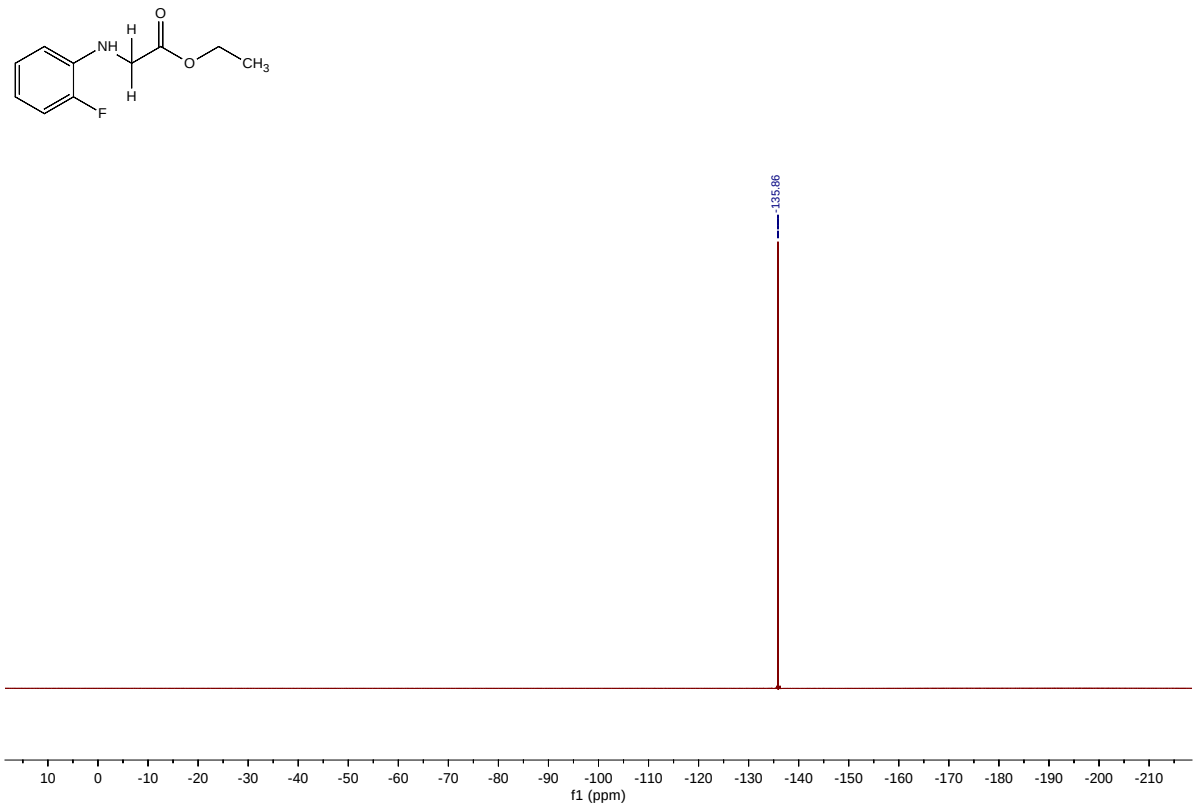


Figure S16: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of ethyl [(2-fluorophenyl)amino]acetate isolated by column chromatography from reaction between 2-fluoroaniline and EDA (Table 6, entry 6).

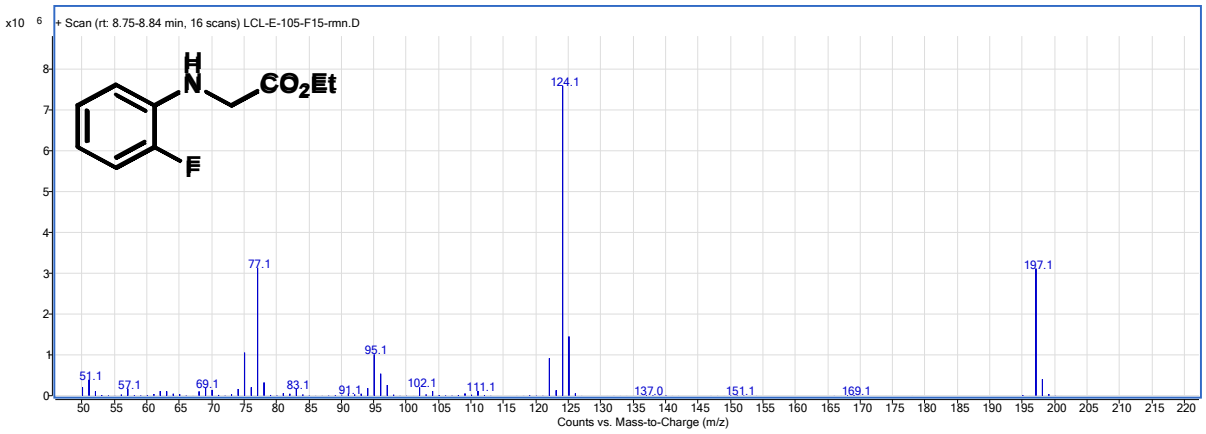
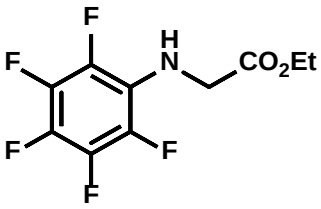


Figure S17: Mass spectrum (EI) of ethyl [(2-fluorophenyl)amino]acetate isolated by column chromatography from reaction between 2-fluoroaniline and EDA (Table 6, entry 6).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_200609_12_E101.d		
Method	Tune_pos_Standard.m	Acquisition Date	6/9/2020 4:16:08 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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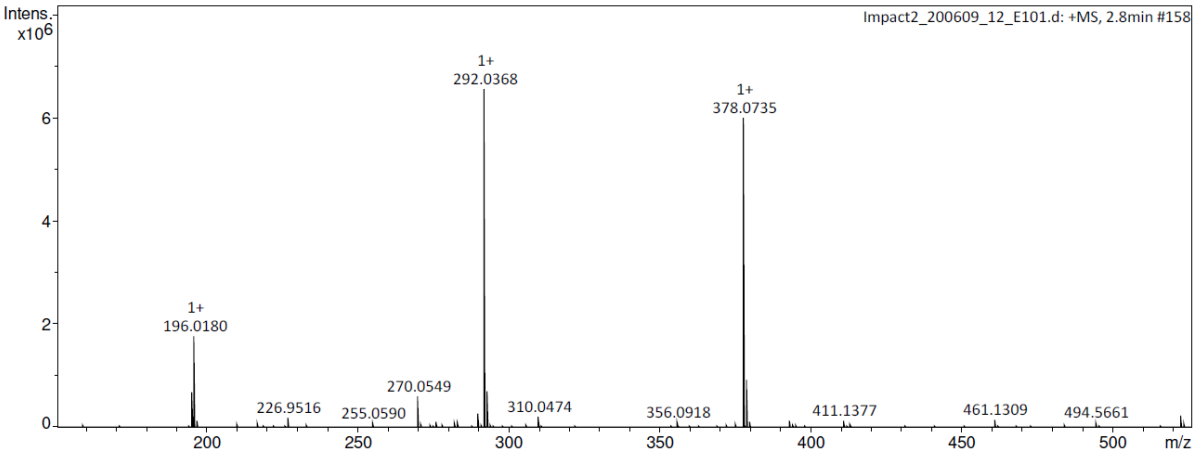

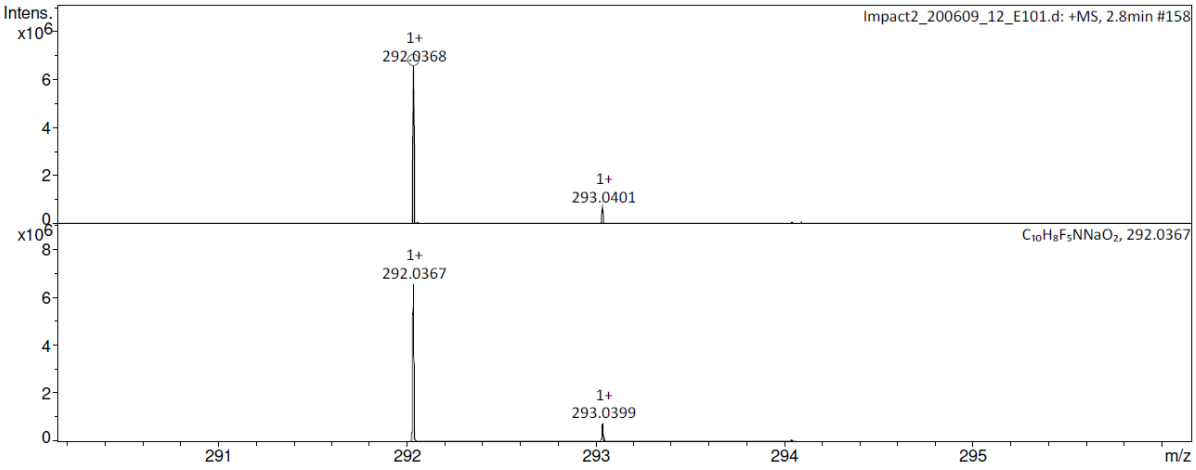

Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
270.0549	C10H9F5NO2	270.0548	C10H8F5NO2	-0.3	7.7	M+H	1+
292.0368	C10H8F5NNaO2	292.0367		-0.1	4.7	M+Na	1+

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Figure S18: HRMS spectrum of ethyl [(2,3,4,5,6-pentafluorophenyl)amino]acetate isolated by column chromatography from reaction between 2,3,4,5,6-pentafluoroaniline and EDA (Table 6, entry 8).

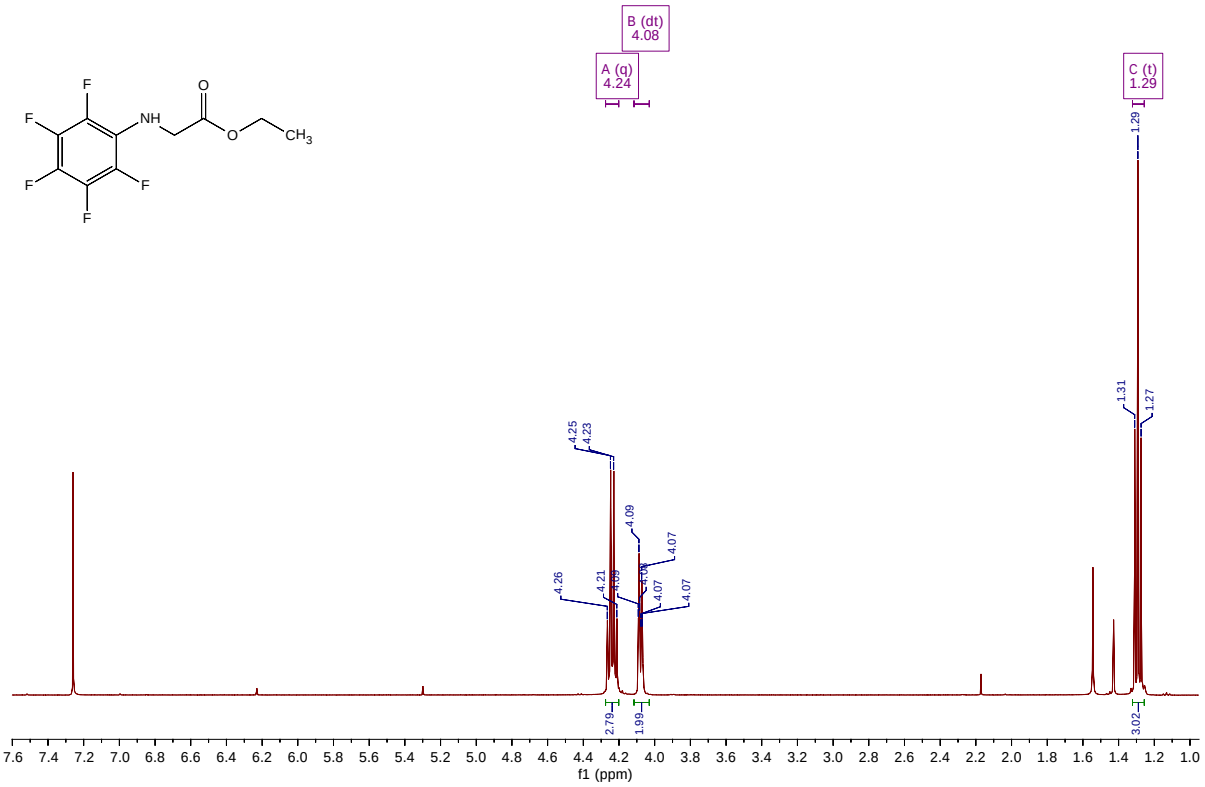


Figure S19: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl [(2,3,4,5,6-pentafluorophenyl)amino]acetate isolated by column chromatography from reaction between 2,3,4,5,6-pentafluoroaniline and EDA (Table 6, entry 8).

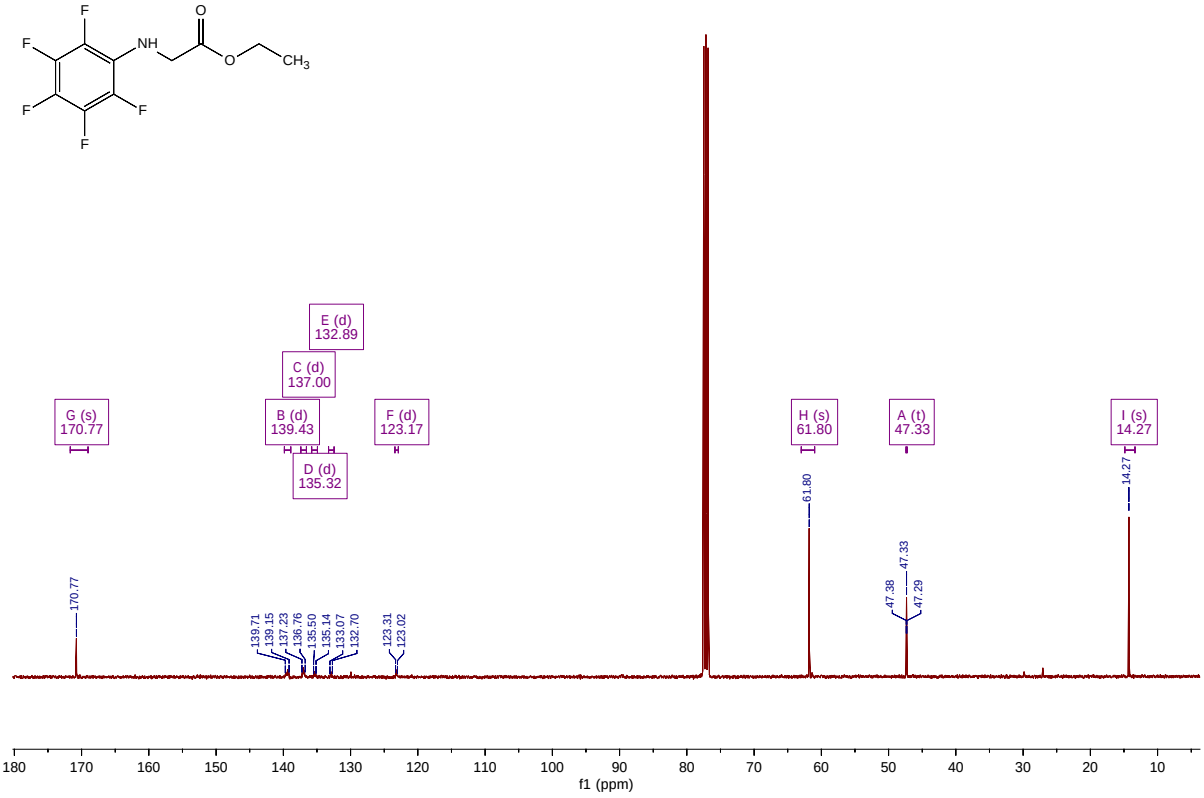


Figure S20: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of ethyl [(2,3,4,5,6-pentafluorophenyl)amino]acetate isolated by column chromatography from reaction between 2,3,4,5,6-pentafluoroaniline and EDA (Table 6, entry 8).

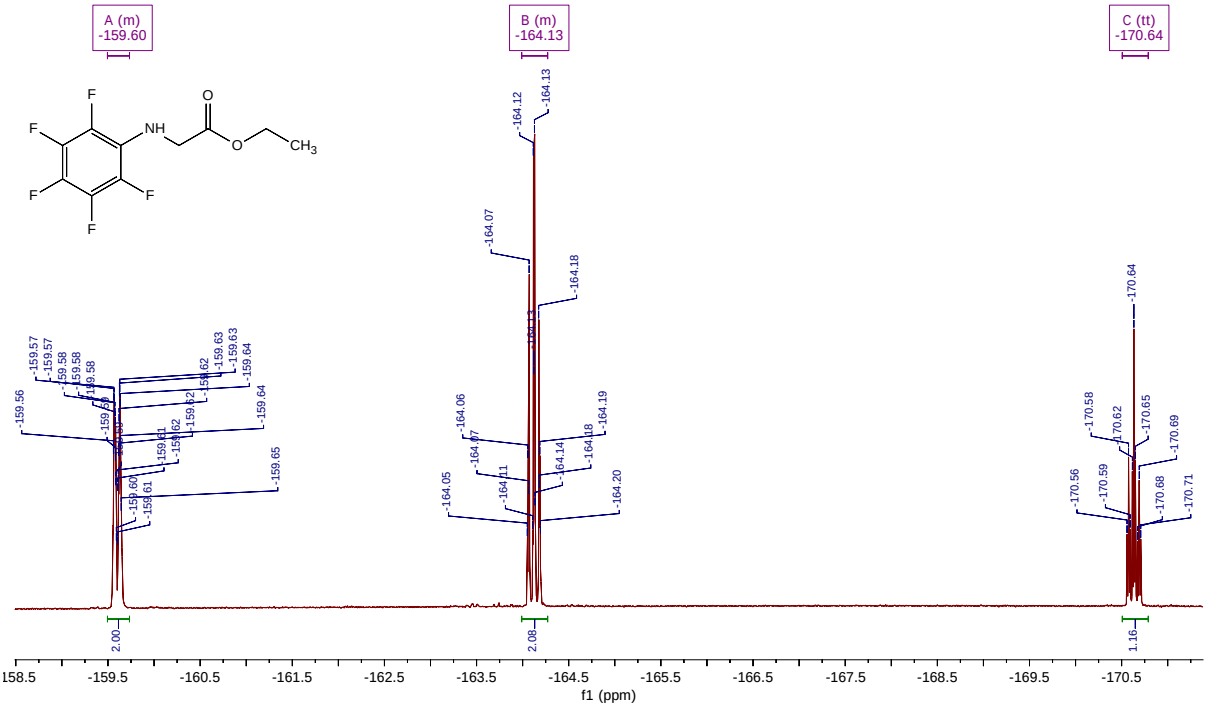


Figure S21: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of ethyl [(2,3,4,5,6-pentafluorophenyl)amino]acetate isolated by column chromatography from reaction between 2,3,4,5,6-pentafluoroaniline and EDA (Table 6, entry 8).

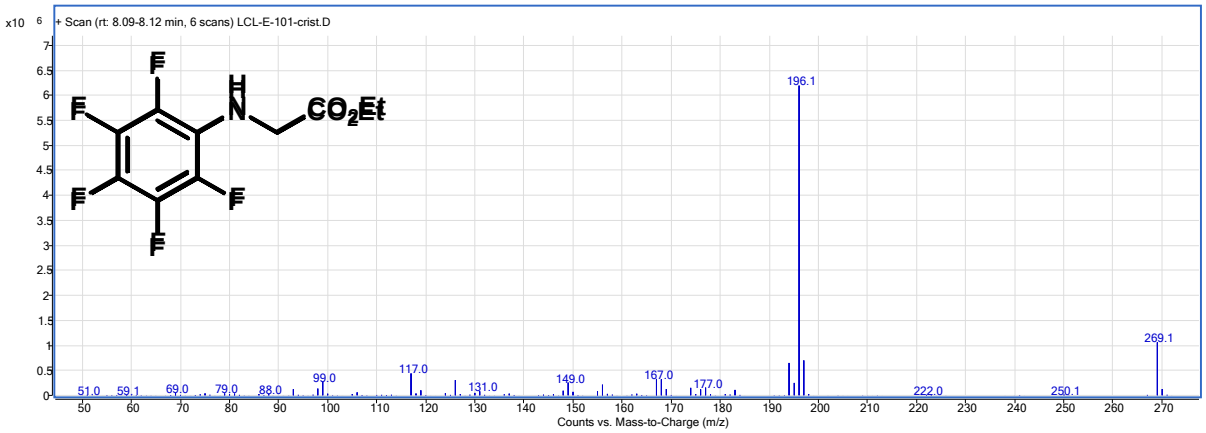
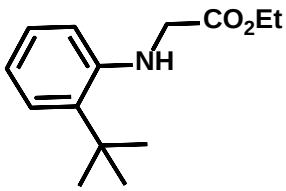


Figure S22: Mass spectrum (EI) of ethyl [(2,3,4,5,6-pentafluorophenyl)amino]acetate isolated by column chromatography from reaction between 2,3,4,5,6-pentafluoroaniline and EDA (Table 6, entry 8).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_200609_15_E108-F11-13.d		
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Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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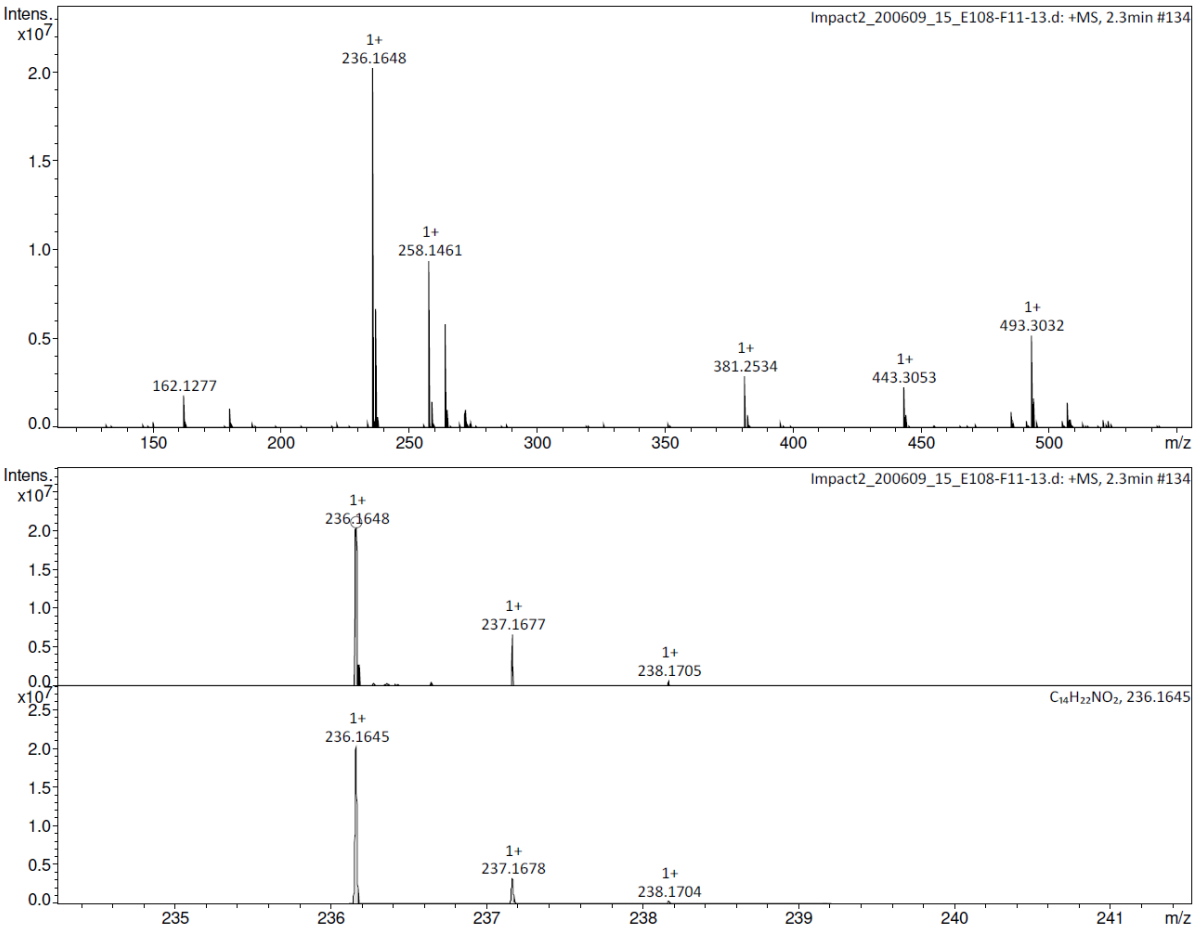
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
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258.1461	C14H21NNaO2	258.1464		1.2	2.0	M+Na	1+

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Figure S23: HRMS spectrum of ethyl [(2-*tert*-butylphenyl)amino]acetate isolated by column chromatography from reaction between 2-*tert*-butylaniline and EDA (Table 6, entry 11).

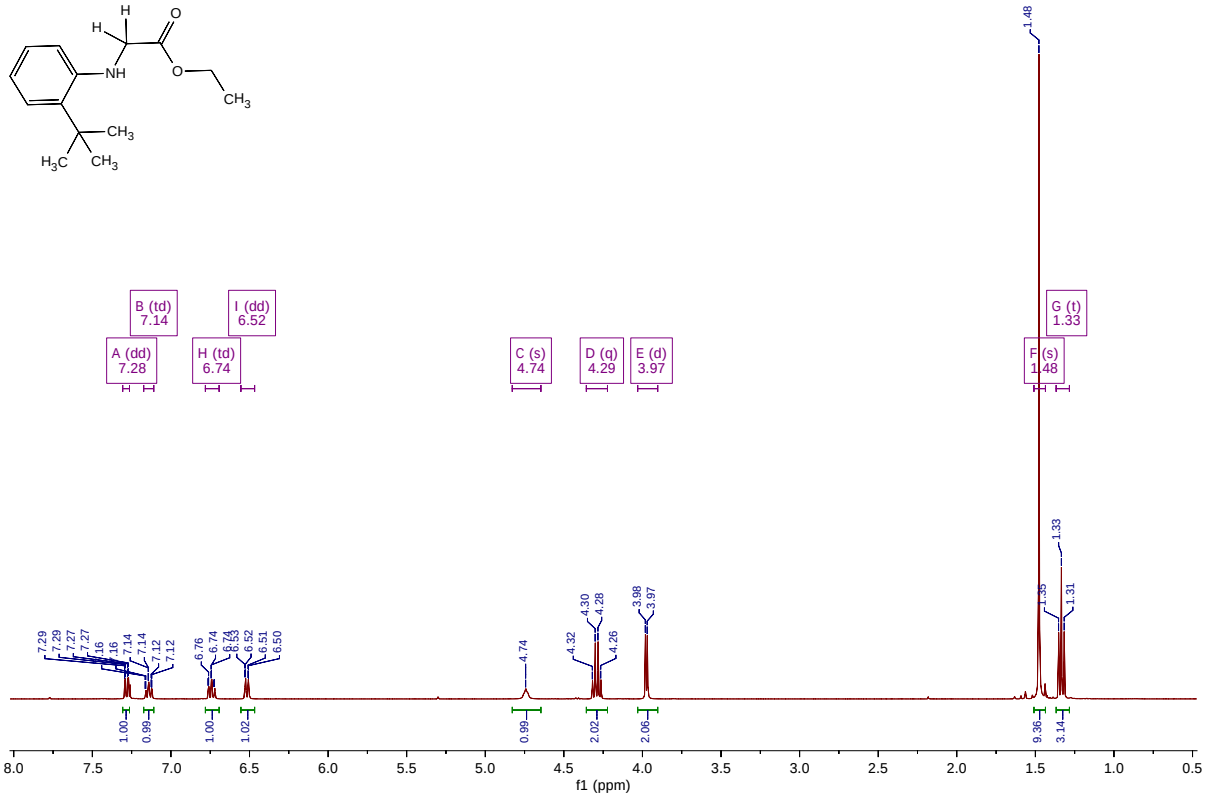


Figure S24: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl [(2-*tert*-butylphenyl)amino]acetate isolated by column chromatography from reaction between 2-*tert*-butylaniline and EDA (Table 6, entry 11).

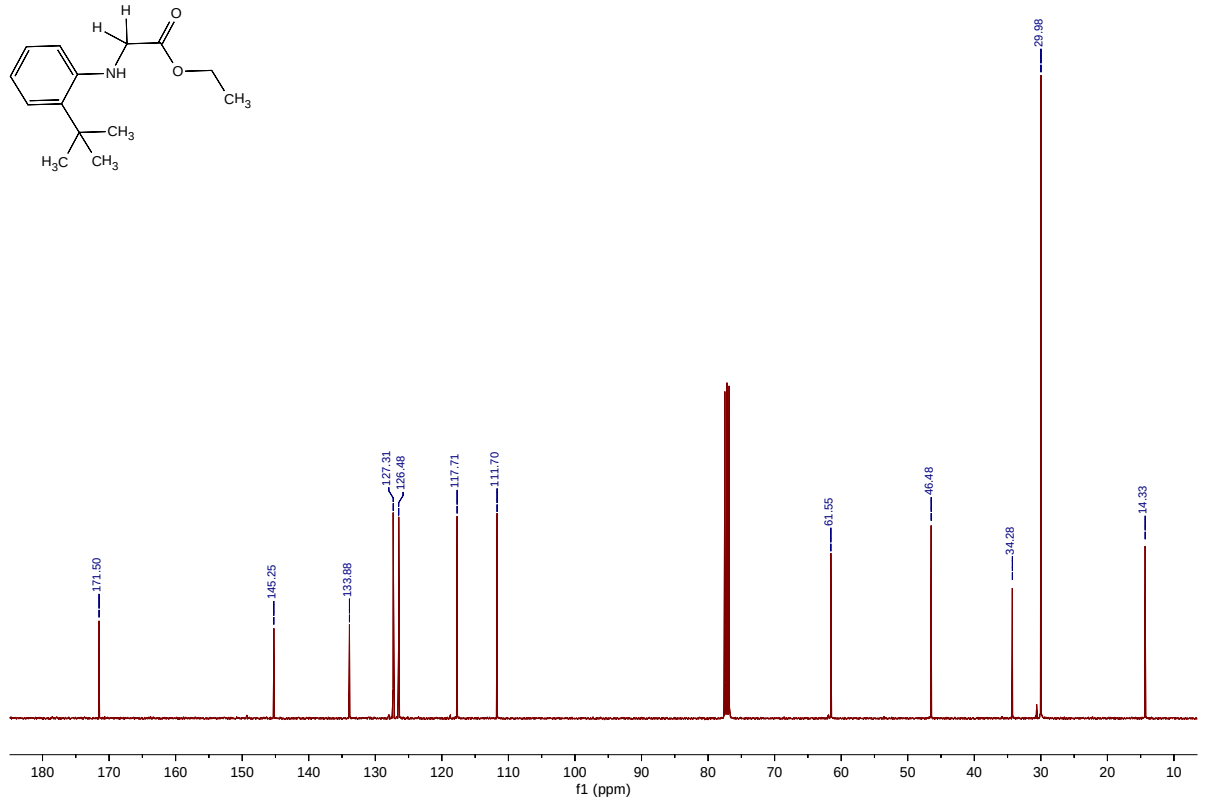


Figure S25: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of ethyl [(2-*tert*-butylphenyl)amino]acetate isolated by column chromatography from reaction between 2-*tert*-butylaniline and EDA (Table 6, entry 11).

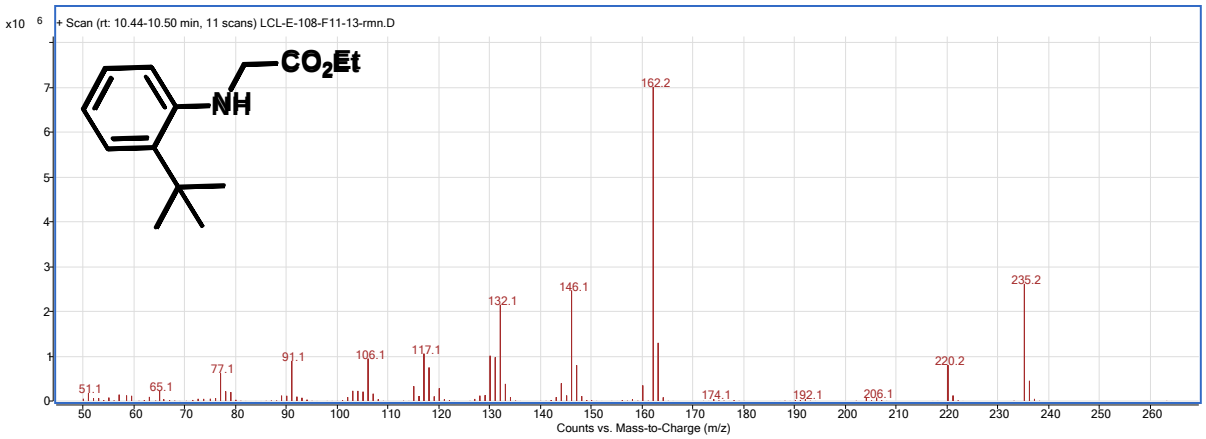
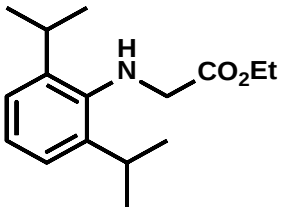


Figure S26: Mass spectrum (EI) of ethyl [(2-*tert*-butylphenyl)amino]acetate isolated by column chromatography from reaction between 2-*tert*-butylaniline and EDA (Table 6, entry 11).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

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Acquisition Parameter

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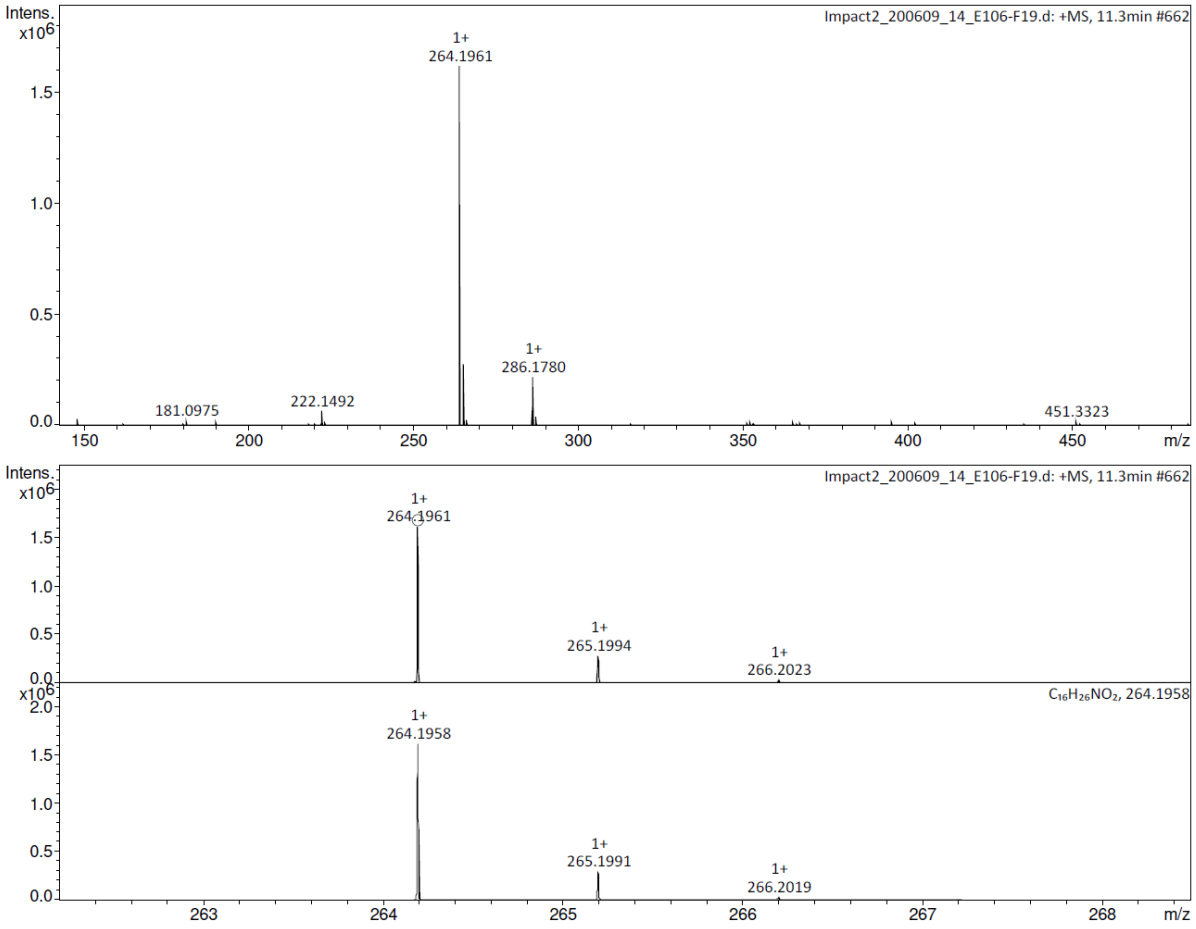
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
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286.1780	C16H25NNaO2	286.1777		-0.9	6.0	M+Na	1+

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Figure S27: HRMS spectrum of ethyl [(2,6-diisopropylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-diisopropylaniline and EDA (Table 6, entry 10).

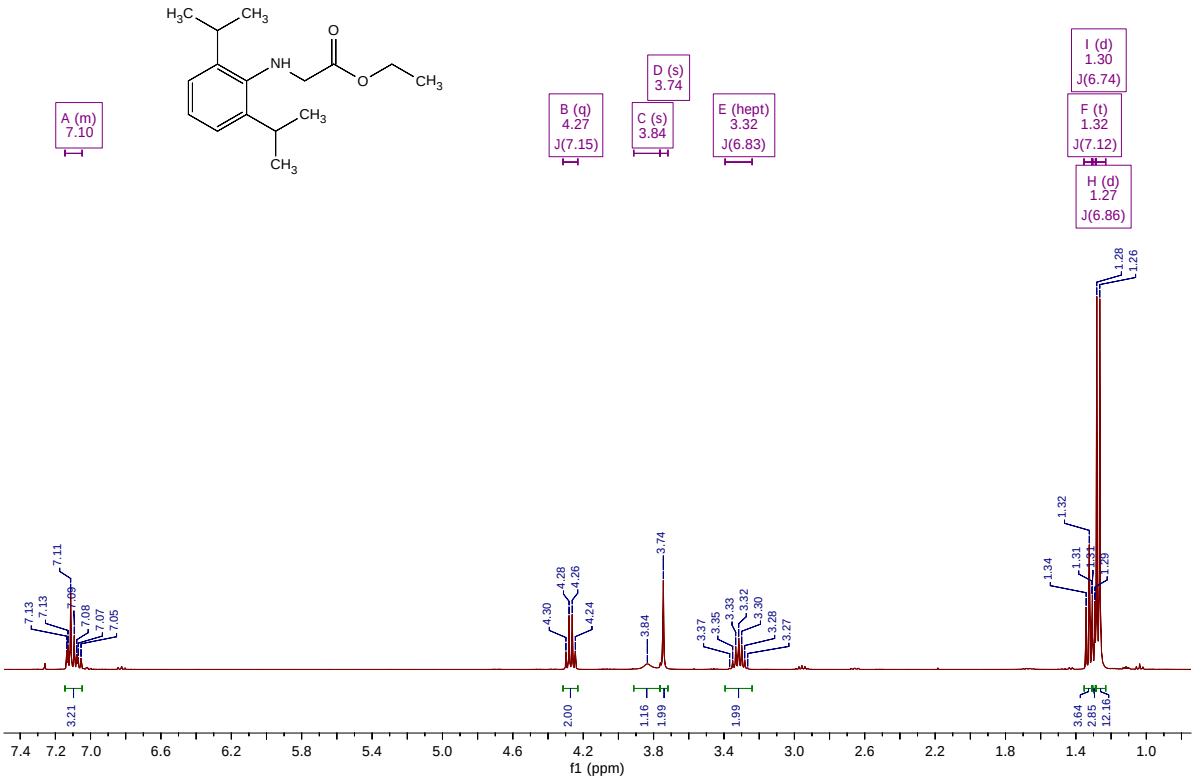


Figure S28: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl [(2,6-diisopropylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-diisopropylaniline and EDA (Table 6, entry 10).

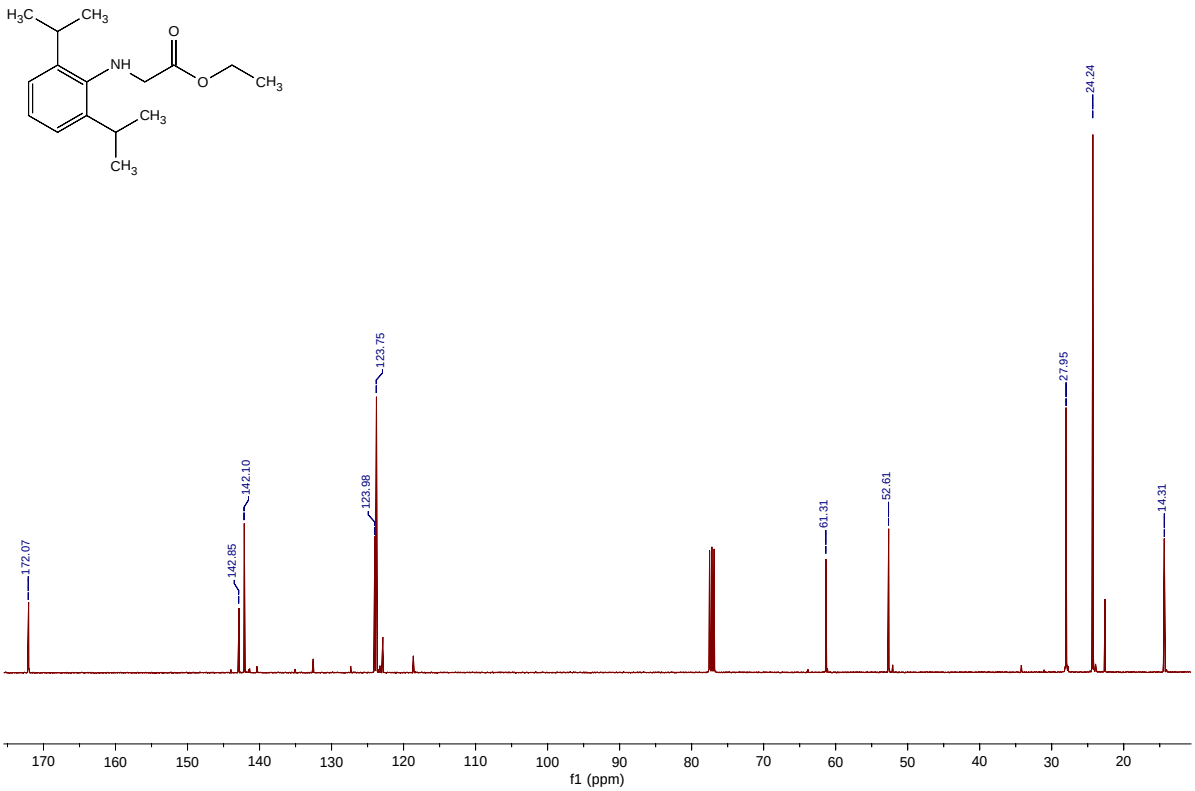


Figure S29: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of ethyl [(2,6-diisopropylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-diisopropylaniline and EDA (Table 6, entry 10).

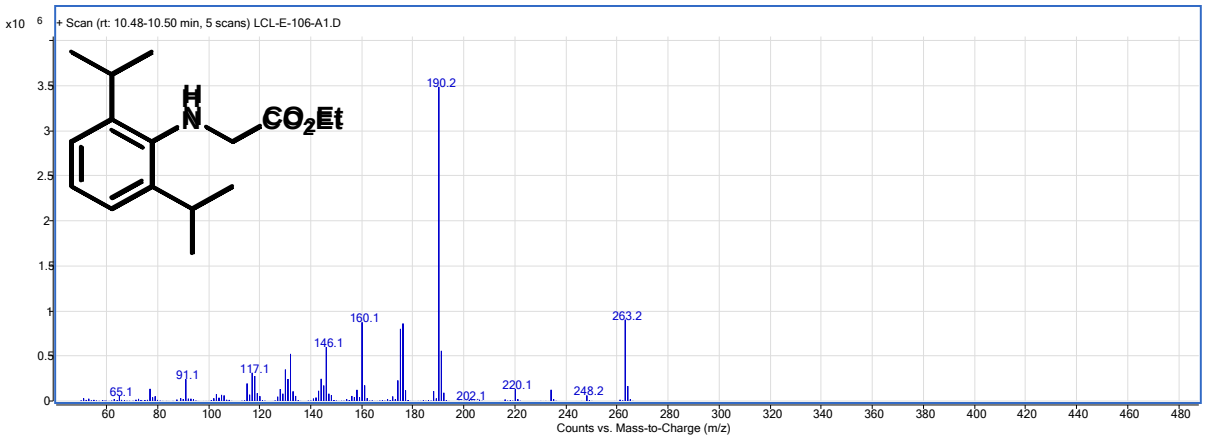
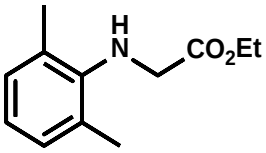


Figure S30: Mass spectrum (EI) of ethyl [(2,6-diisopropylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-diisopropylaniline and EDA (Table 6, entry 10).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_200609_17_E109-F12-17.d		
Method	Tune_pos_Standard.m	Acquisition Date	6/9/2020 5:09:15 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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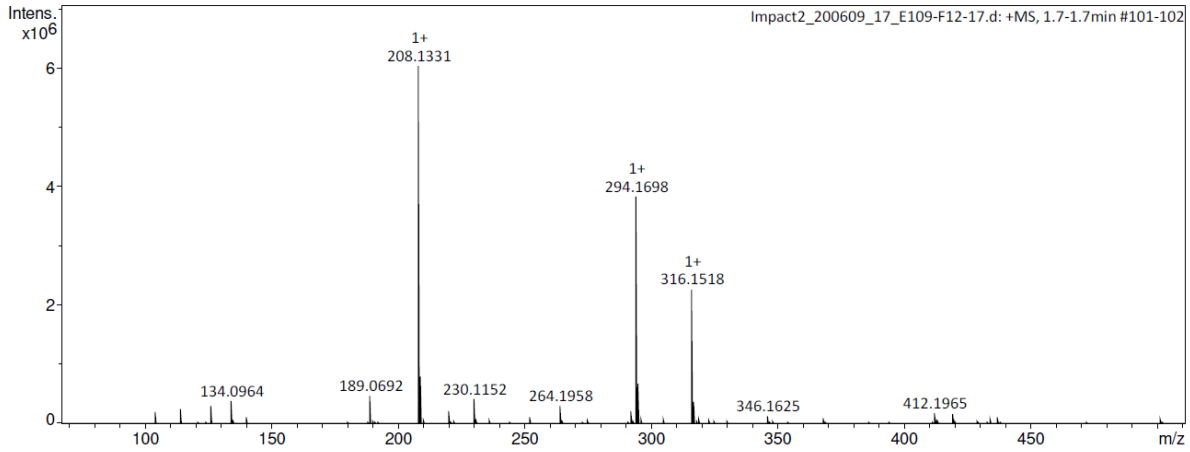
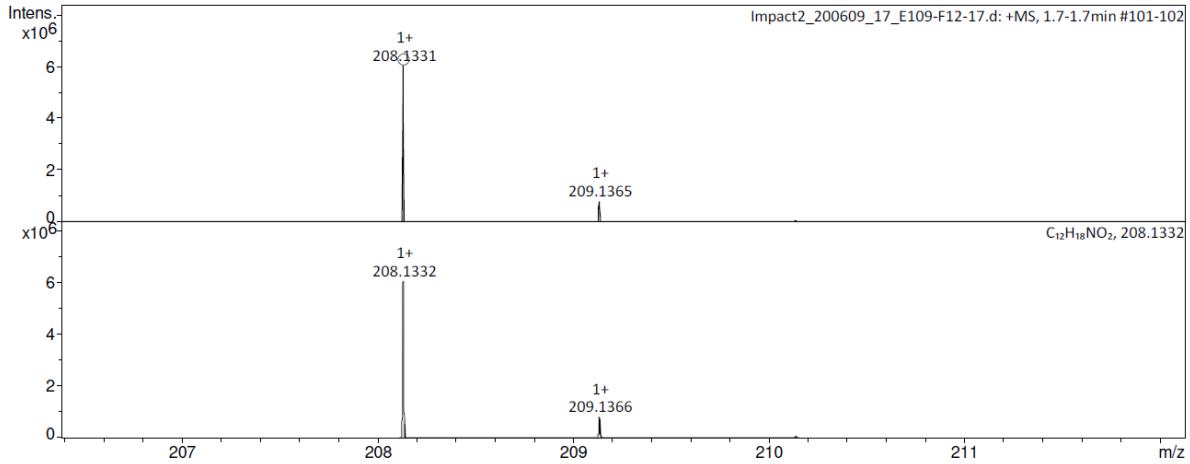
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
208.1331	C12H18NO2	208.1332	C12H17NO2	0.5	3.5	M+H	1+

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Figure S31: HRMS spectrum of ethyl [(2,6-dimethylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-dimethylaniline and EDA (Table 6, entry 9).

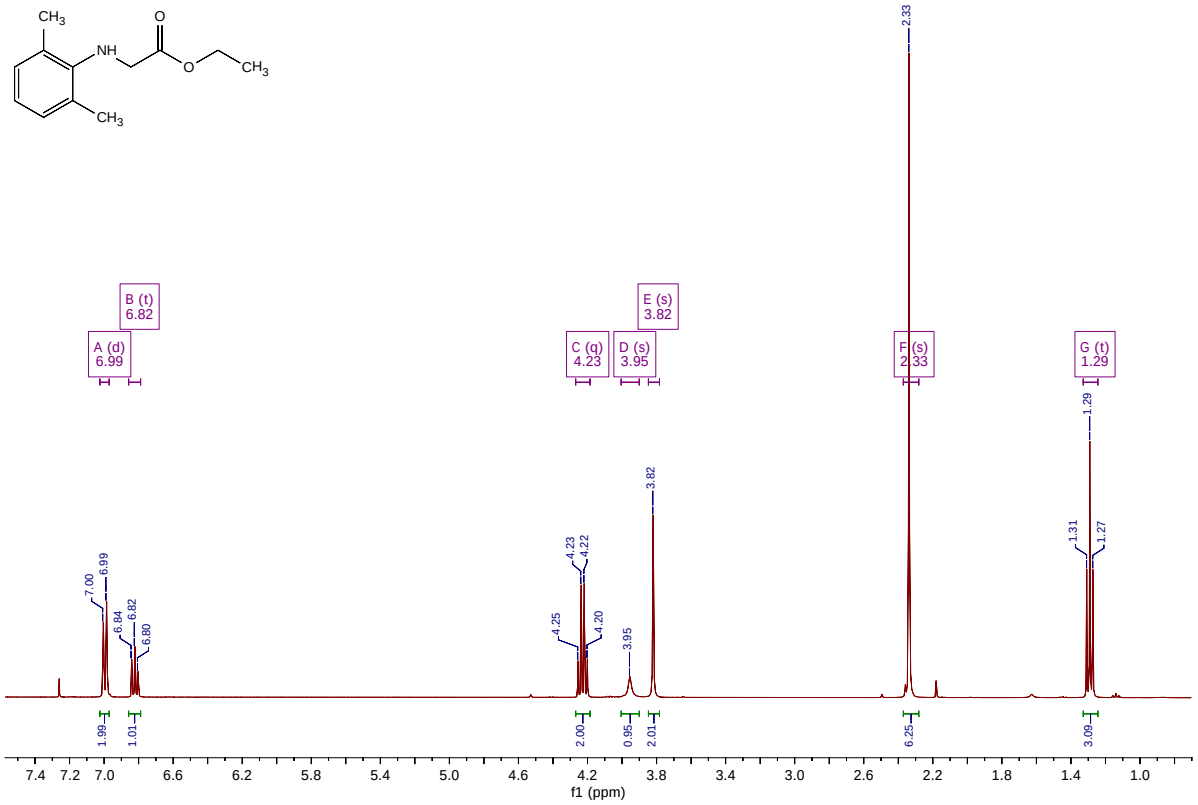


Figure S32: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl [(2,6-dimethylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-dimethylaniline and EDA (Table 6, entry 9).

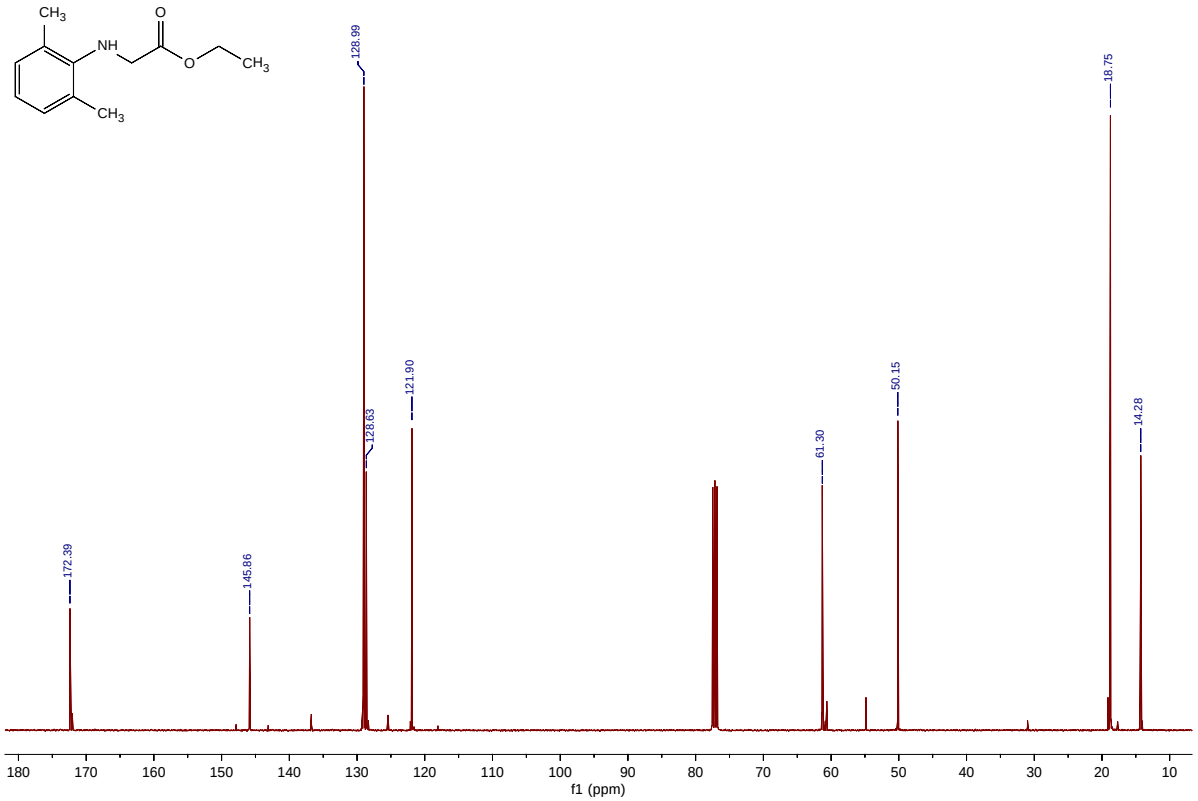


Figure S33: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of ethyl [(2,6-dimethylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-dimethylaniline and EDA (Table 6, entry 9).

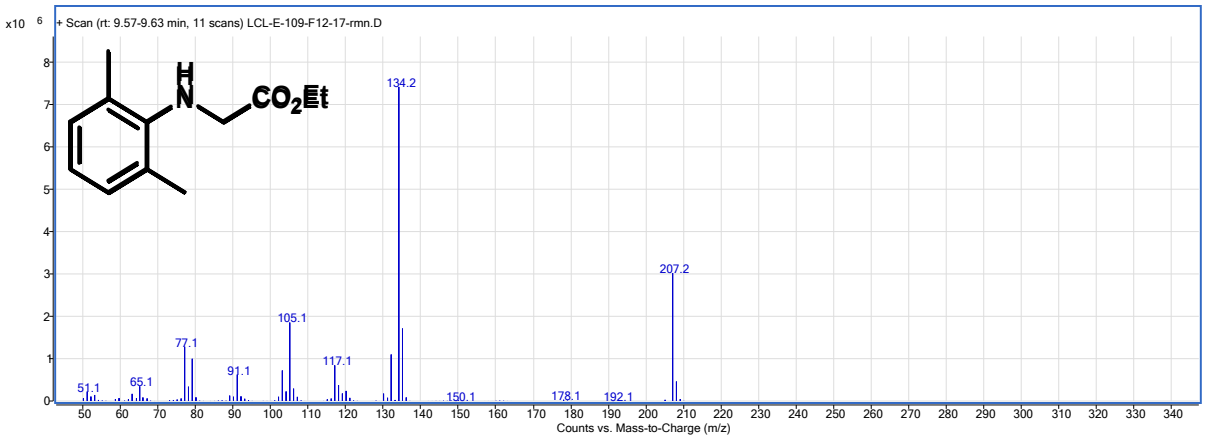
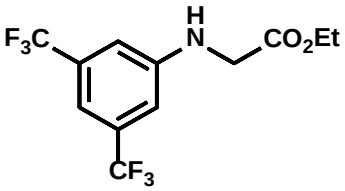


Figure S34: Mass spectrum (EI) of ethyl [(2,6-dimethylphenyl)amino]acetate isolated by column chromatography from reaction between 2,6-dimethylaniline and EDA (Table 6, entry 9).



CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

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Acquisition Parameter

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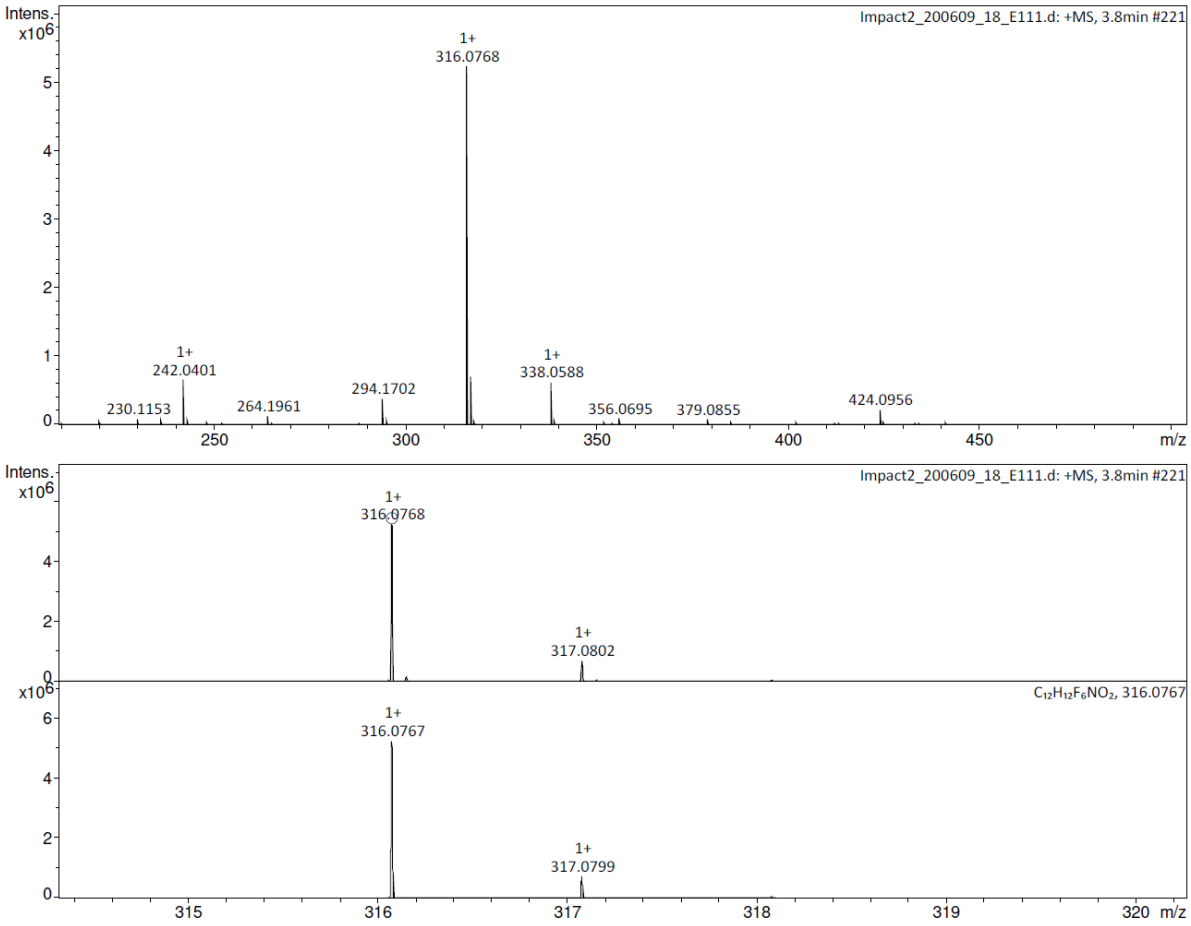
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
316.0768	C12H12F6NO2	316.0767	C12H11F6NO2	-0.4	1.3	M+H	1+
338.0588	C12H11F6NNaO2	338.0586		-0.7	9.8	M+Na	1+

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Figure S35: HRMS spectrum of ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate isolated by column chromatography from reaction between 3,5-bis(trifluoromethyl)aniline and EDA (Table 6, entry 7).

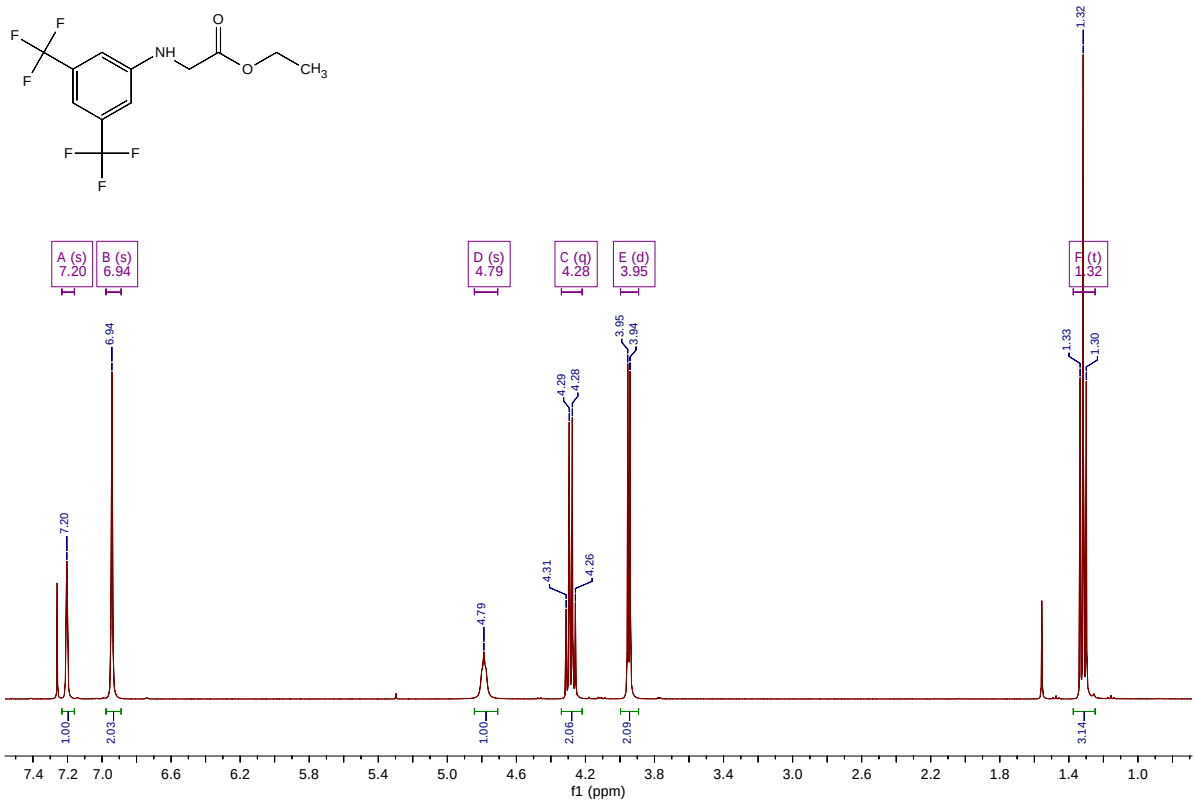


Figure S36: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate isolated by column chromatography from reaction between 3,5-bis(trifluoromethyl)aniline and EDA (Table 6, entry 7).

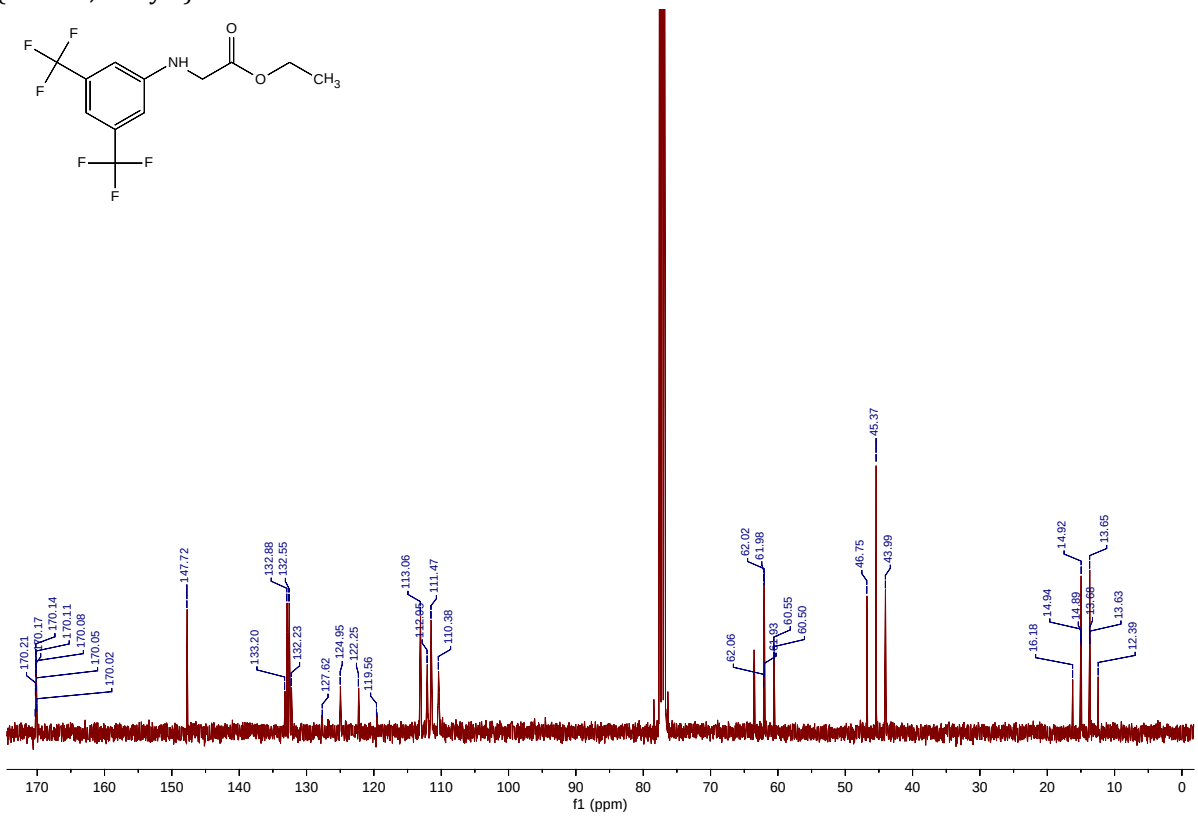


Figure S37: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate isolated by column chromatography from reaction between 3,5-bis(trifluoromethyl)aniline and EDA (Table 6, entry 7).

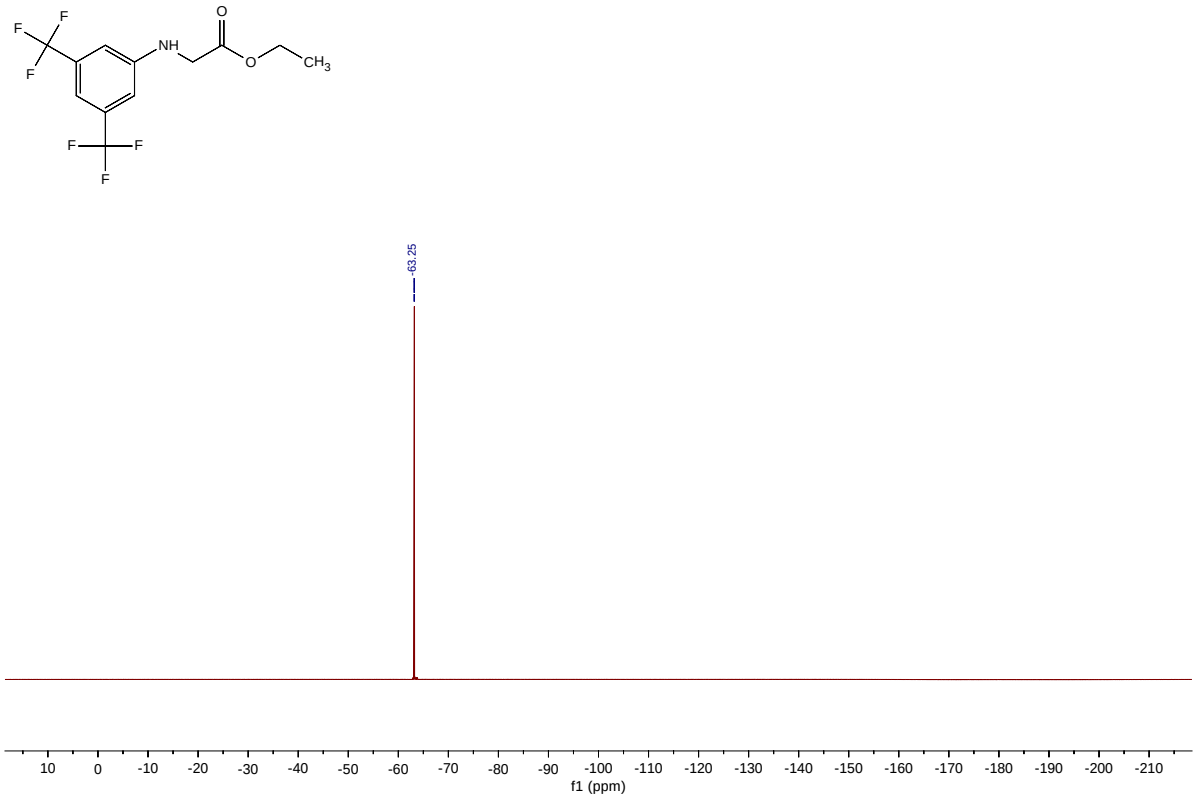


Figure S38: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate isolated by column chromatography from reaction between 3,5-bis(trifluoromethyl)aniline and EDA (Table 6, entry 7).

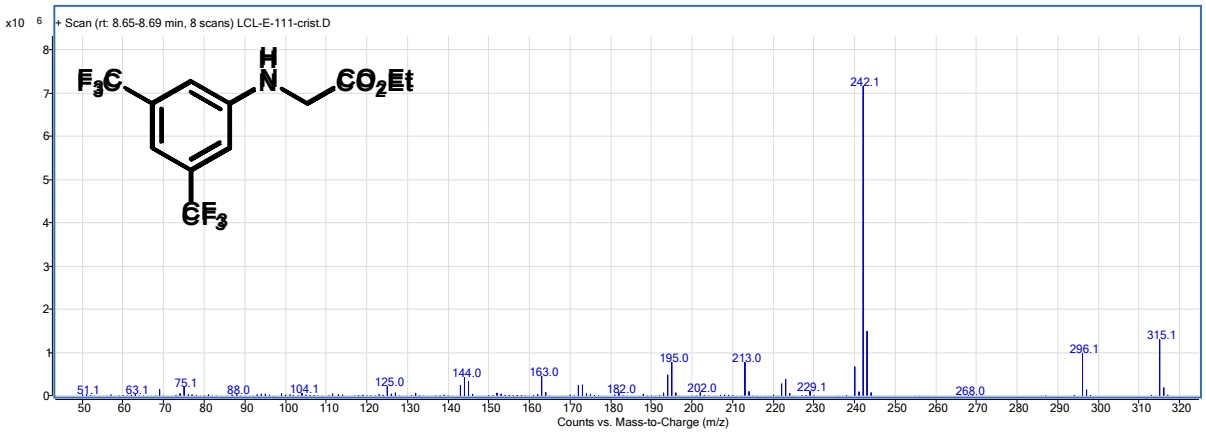
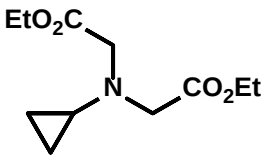


Figure S39: Mass spectrum (EI) of ethyl {[3,5-bis(trifluoromethyl)phenyl]amino}acetate isolated by column chromatography from reaction between 3,5-bis(trifluoromethyl)aniline and EDA (Table 6, entry 7).



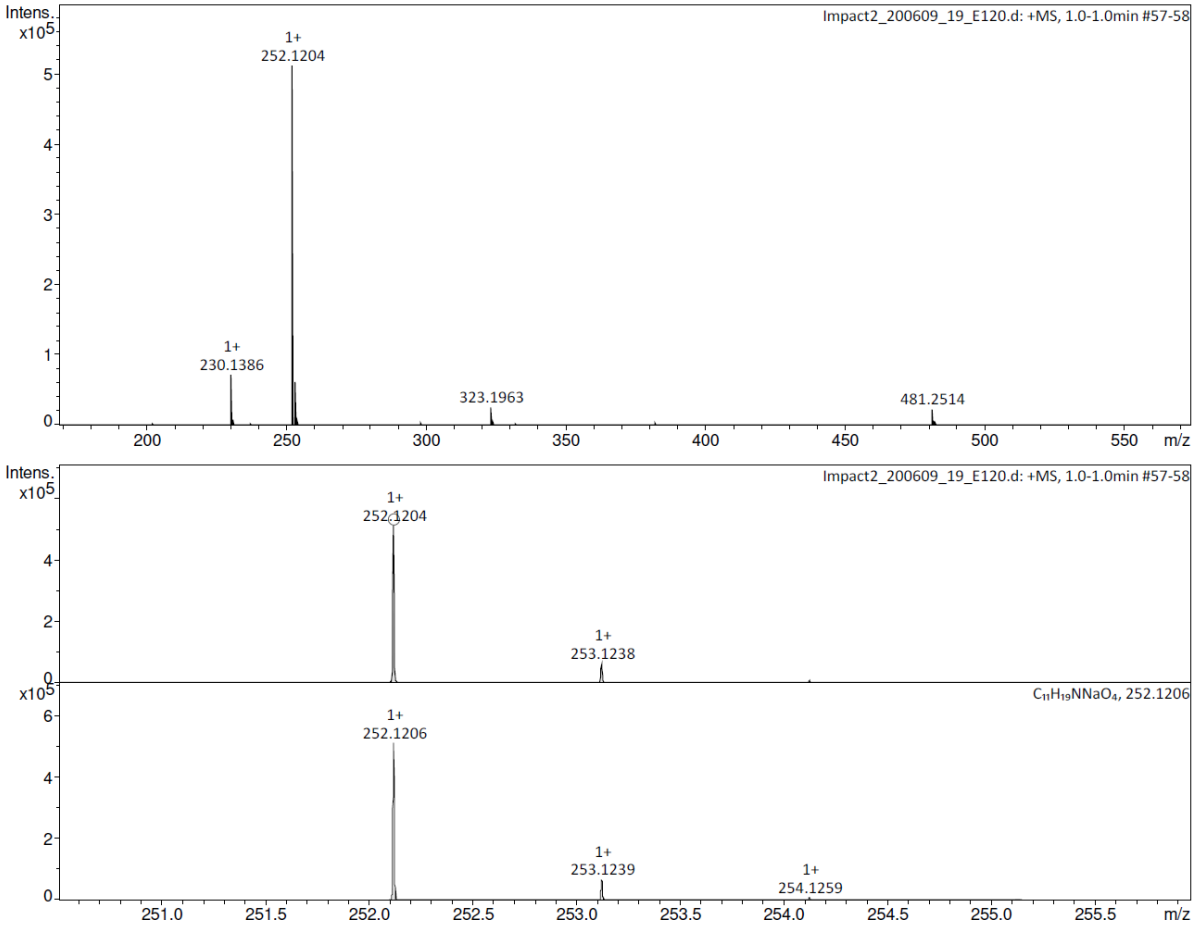
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_200609_19_E120.d		
Method	Tune_pos_Standard.m	Acquisition Date	6/9/2020 5:57:41 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
230.1386	C11H20NO4	230.1387	C11H19NO4	0.3	5.8	M+H	1+
252.1204	C11H19NNaO4	252.1206		1.0	3.8	M+Na	1+
481.2514	C22H38N2NaO8	481.2520	C22H38N2O8	1.3	22.4	M+Na	1+

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Figure S40: HRMS spectrum of N-(2-ethoxy-2-oxoethyl)-N-(cyclopropyl)glycine ethyl ester isolated by column chromatography from reaction between cyclopropylamine and EDA (Table 6, entry 21).

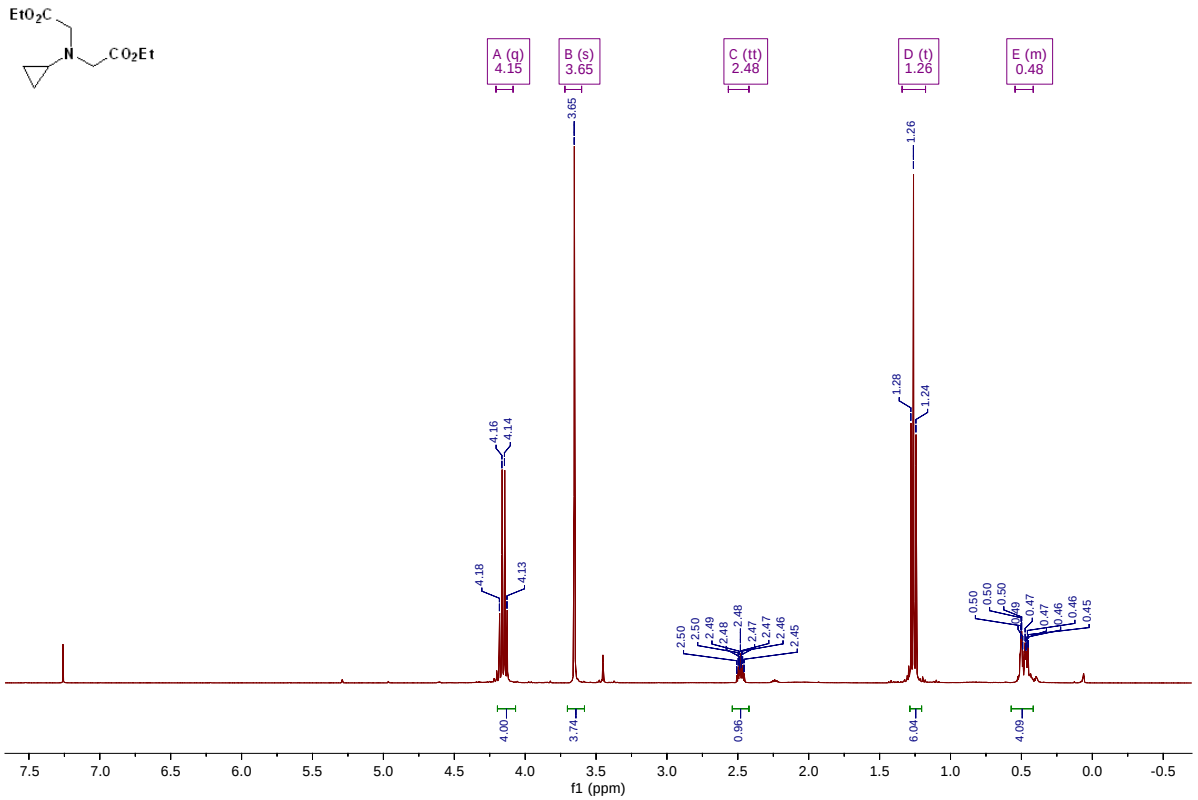

Figure S41: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of N-(2-ethoxy-2-oxoethyl)-N-(cyclopropyl)glycine ethyl ester isolated by column chromatography from reaction between cyclopropylamine and EDA (Table 6, entry 21).

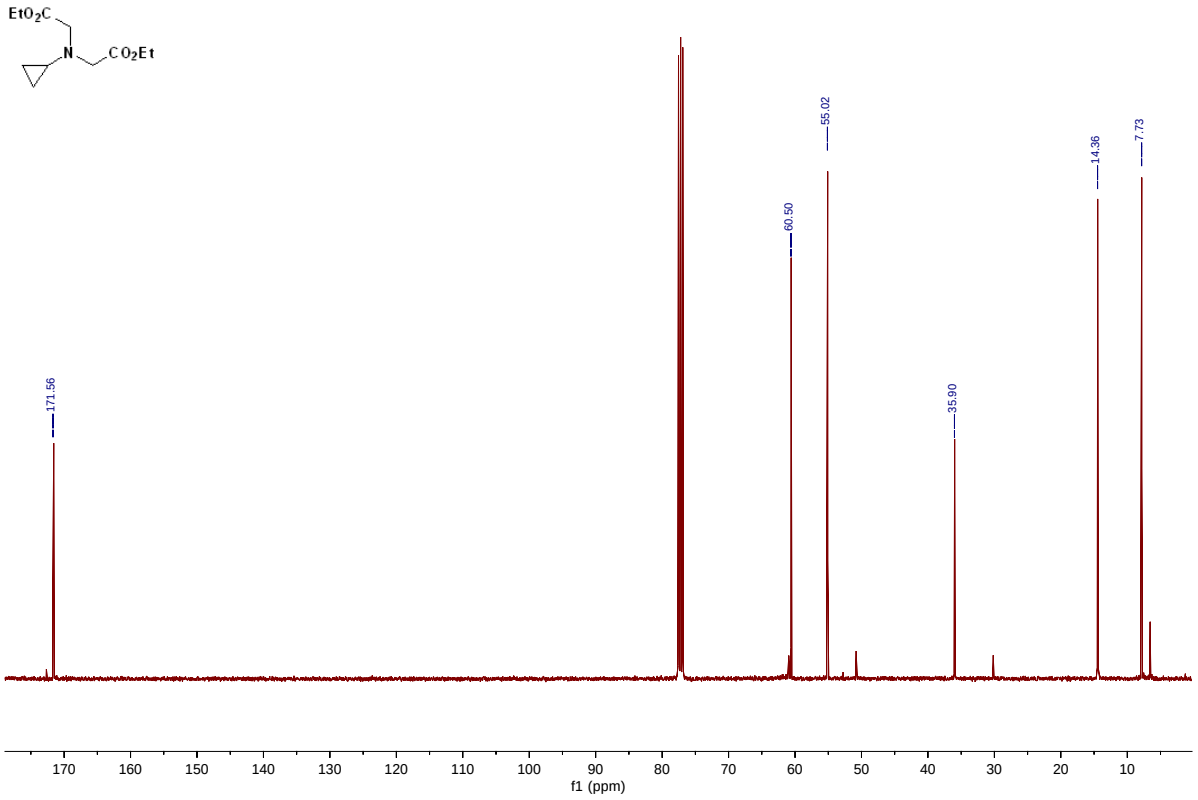

Figure S42: ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of N-(2-ethoxy-2-oxoethyl)-N-(cyclopropyl)glycine ethyl ester isolated by column chromatography from reaction between cyclopropylamine and EDA (Table 6, entry 21).

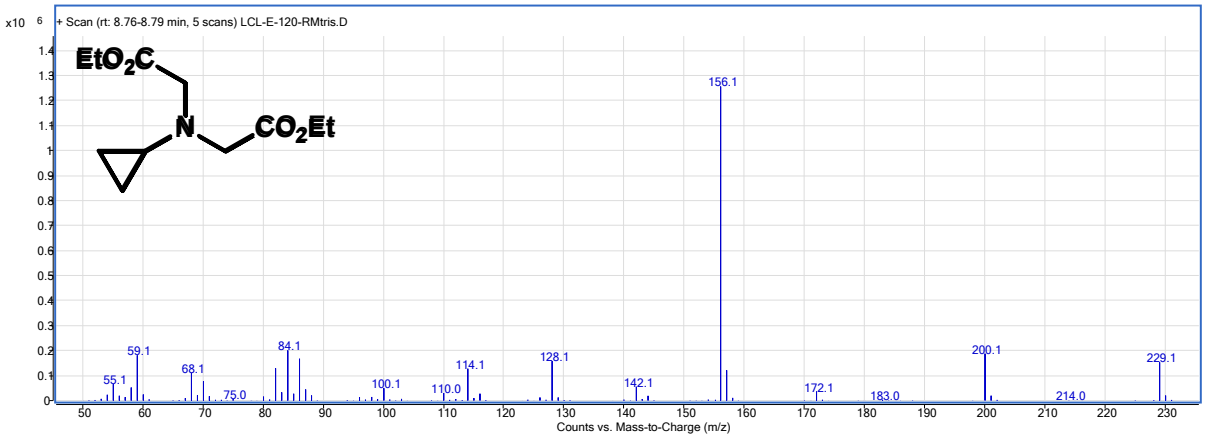

Figure S43: Mass spectrum (EI) of N-(2-ethoxy-2-oxoethyl)-N-(cyclopropyl)glycine ethyl ester isolated by column chromatography from reaction between cyclopropylamine and EDA (Table 6, entry 21).