

Supplementary information

Hydrogenation of nitrile to primary amine with carbon-coated Ni/NiO@C catalyst under mild conditions

Weidong Liu, Jianguo Liu*

School of Energy and Environment, Southeast University, Nanjing 210096.

* Corresponding author's e-mail: liujg@seu.edu.cn

Table S1. Catalytic hydrogenation of nitrile over a series of reported catalysts.

Catalyst	Reaction Condition	Con(%)	Sel(%)	Runs	Ref.
Ni/SiC	1 mmol (substrate), methanol (20 mL), 100 mg (catalyst), 2MPa H ₂ , 150°C, 2h	99	85	5	¹
Ni ₃ P/SiO ₂	8 mmol (substrate), methanol (30 mL), methanol-ammonia solution (10 mL, NH ₃ : 7M), 25 mg (catalyst), 4 MPa H ₂ , 130°C, 3 h	100	100		²
Ni/SiO ₂	0.12 mol L ⁻¹ (substrate), ethanol (150 mL), 1 g(catalyst), 1.3 MPa H ₂ , 100°C	100	77.3	18h	³
P-MOLCoRh	0.2 mmol (substrate), THF (1 mL), 0.2mol% (catalyst), 5 MPa H ₂ , 100°C, 72 h	Yield=74%			⁴
Ni-1.5Re/SiO ₂	0.11 g (substrate), CH ₃ OH (4.5 mL), 0.05g (catalyst), NH ₃ · H ₂ O (0.5 mL), 1.0 MPa H ₂ , 120°C, 1.5h	>99	>99	1300h	⁵
Cu@AmHMSiO ₂ @C	1mmol (substrate), methanol (2 mL), 20mg (catalyst), 0.2 g ammonia borane, 60°C, 0.5h	100	96	5	⁶
Cu@NC-ZrO ₂ -600	1mmol (substrate), methanol (2 mL), 20mg (catalyst), 0.1 g ammonia borane, 60°C, 3h	95	100	5	⁷
nano-Ni ₃ C/Al ₂ O ₃	0.1 mol% Ni, 2-propanol, NH ₃ aq., 4.5 MPa H ₂ , 150°C, 40 h	Yield=90%		3	⁸
Ni-NPs@SiO ₂ -500	10 mmol (substrate), MeOH(40 mL), 320mg (catalyst, 4.8 mol% Ni), 3.5 MPa H ₂ , 0.5MPa NH ₃ , 60°C, 20 h	>99	87	8	⁹
Pd _n /ND@G	0.5mmol(substrate), methanol (10 mL), 10mg (catalyst), 3mmol ammonia borane(0.1 MPa), 40°C, 0.5h	>99	>98		¹⁰
Co ₂ P NR/HT	0.5mmol(substrate), NH ₃ aq(1.2 mL), 2-propanol (3.0 mL), 2.5 mol % Co, 4.0 MPa H ₂ , 130°C, 1 h	Yield=93%		5	¹¹
MC/Ni	1mmol(substrate), MeOH (10 mL), NH ₃ · H ₂ O (36 wt.%, 200 mL, 2.8 mmol), 20mg (catalyst), 0.25 MPa H ₂ , 80°C, 6h	100	>99	6	¹²
Pd-Cu _{0.5} /Fe ₃ O ₄	1mmol(substrate), methanol (2 mL), 10 wt% of substrate (catalyst), 3mmol ammonia borane, 40°C, 1.5h	>99	95	5	¹³
Pd0.6Ni@S-1	0.5mmol(substrate), methanol (2 mL), 5 mg (catalyst), 80°C, 2 bar H ₂ , 2 h	>99	92		¹⁴

Ni/NiO@C-600-200-1-H ₂ O	5 mmol(substrate), methanol-ammonia solution (5 mL, NH ₃ : 2 M), 10 mg (catalyst), 1 MPa H ₂ , 120 °C, 4 h	> 99	98	10	This work
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References

1. Z.-F. Jiao, Z.-Y. Zheng, J.-X. Zhao, C.-D. Zhang, T.-Y. Xu and X.-Y. Guo, *New Journal of Chemistry*, 2024, **48**, 3892-3898.
2. K. Lyu, X. Jian, K. Nie, S. Liu, M. Huai, Z. Kang, D. Liu, X. Lan and T. Wang, *Journal of the American Chemical Society*, 2024, **146**, 21623-21633.
3. D. J. Segobia, A. F. Trasarti and C. R. Apesteguía, *Reaction Chemistry & Engineering*, 2021, **6**, 2181-2190.
4. Q. Y. Guo, Z. Wang, Y. Fan, H. Zheng and W. Lin, *Angewandte Chemie International Edition*, 2024, DOI: 10.1002/anie.202409387.
5. Z. Ma, L. Ma, X. Chen, X. Wang, Y. Tan, W. Yang, S. Wang, L. Yan, K. Zhu and Y. Ding, *Chemical Engineering Journal*, 2023, **466**.
6. R. Guo, X. Zhang, Z.-N. Hu, D. Niu, X. Li, H. Sun and Q. Liang, *Journal of Environmental Chemical Engineering*, 2023, **11**.
7. R. Guo, X. Zhang, X. Li, D. Niu and H. Sun, *Journal of the Taiwan Institute of Chemical Engineers*, 2022, **140**.
8. S. Yamaguchi, D. Kiyohira, K. Tada, T. Kawakami, A. Miura, T. Mitsudome and T. Mizugaki, *Chemistry*, 2024, **30**, e202303573.
9. Z. Ma, V. G. Chandrashekar, B. Zhou, A. M. Alenad, N. Rockstroh, S. Bartling, M. Beller and R. V. Jagadeesh, *Chemical Science*, 2022, **13**, 10914-10922.
10. Z. Liu, F. Huang, M. Peng, Y. Chen, X. Cai, L. Wang, Z. Hu, X. Wen, N. Wang, D. Xiao, H. Jiang, H. Sun, H. Liu and D. Ma, *Nat Commun*, 2021, **12**, 6194.
11. M. Sheng, S. Yamaguchi, A. Nakata, S. Yamazoe, K. Nakajima, J. Yamasaki, T. Mizugaki and T. Mitsudome, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 11238-11246.
12. Y. Zhang, H. Yang, Q. Chi and Z. Zhang, *ChemSusChem*, 2019, **12**, 1246-1255.
13. L. Liu, Y. Liu, Y. Ai, J. Li, J. Zhou, Z. Fan, H. Bao, R. Jiang, Z. Hu, J. Wang, K. Jing, Y. Wang, Q. Liang and H. Sun, *iScience*, 2018, **8**, 61-73.
14. Q. Lu, X.-Z. Wei, H. Wang, Q. Zhang, X. Zhang, L. Chen, J. Liu and L. Ma, *Chem. Eng. Sci.*, 2023, **279**.

Table S2.

The conversion and selectivity of phenethylamine over different catalysts for the hydrogenation of phenylacetonitrile. Reaction conditions: 10 mg catalyst, 5 mmol substrate material, 5 mL ammonia methanol solution (2M), 40 bar H₂, 4 h, 90 °C.

Entry	Catalyst	Con.(%)	Sel.(%)
1	Ni@C-600-H ₂ O	0	0
2	Ni/NiO@C-600-200-1-H ₂ O	91.36	92.23

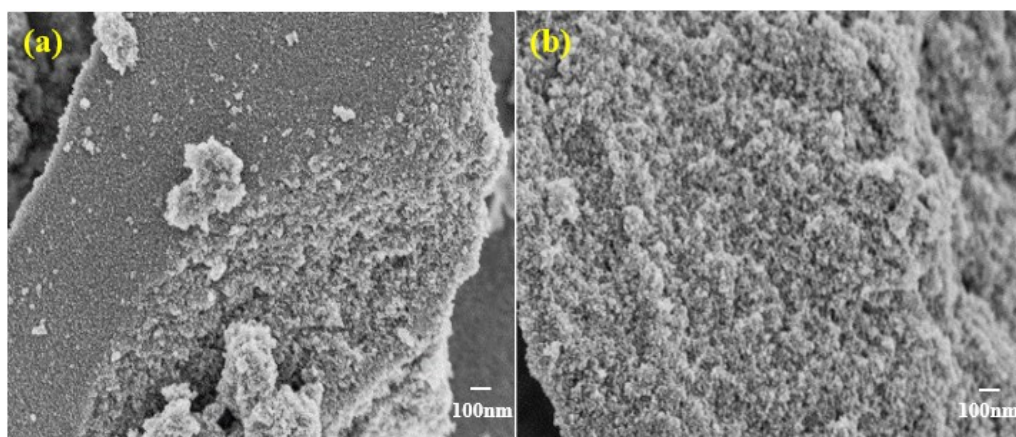


Fig. S1 SEM images of Ni@C-600-H₂O (a), Ni/NiO@C-600-200-1-H₂O (b).

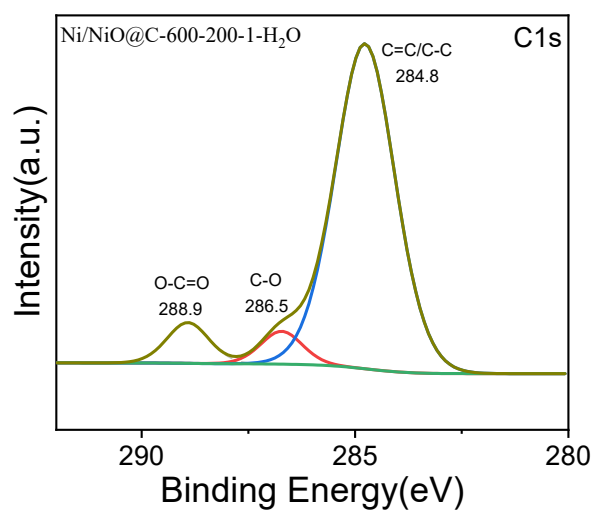
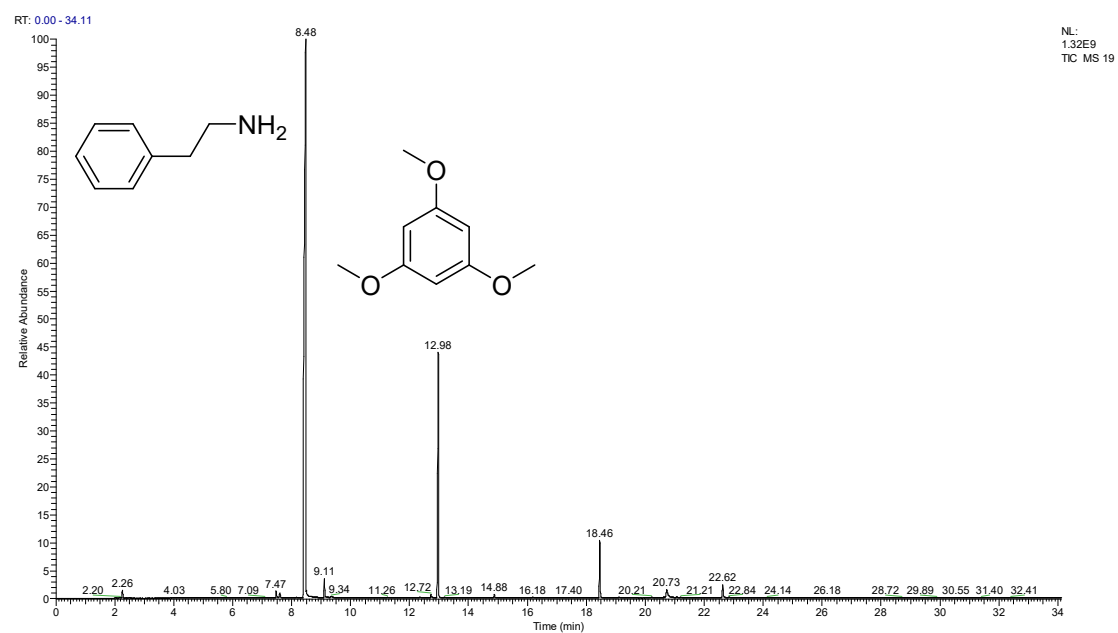
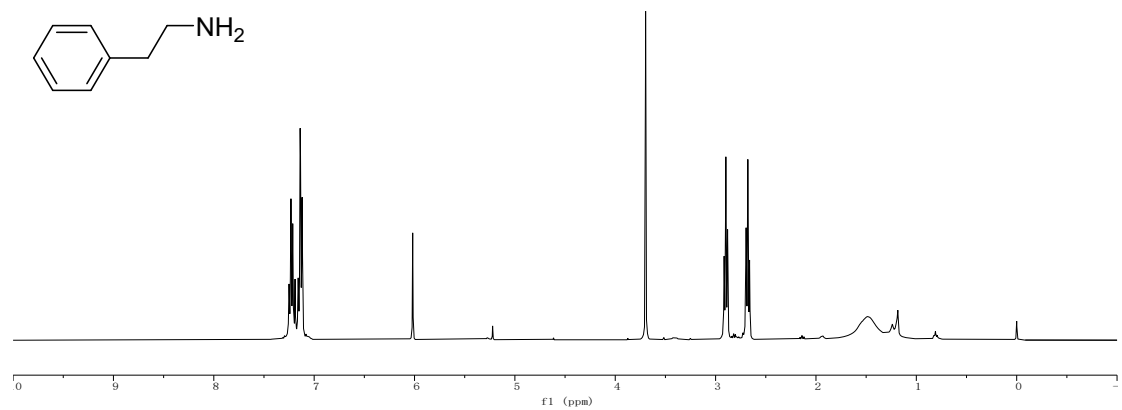


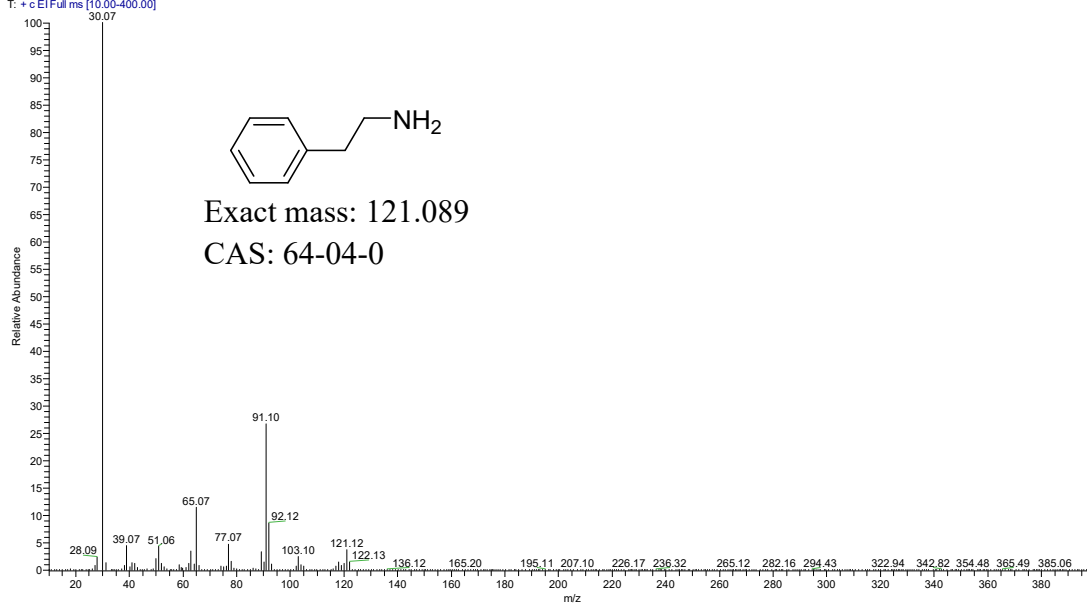
Fig. S2 C 1s spectrum of Ni/NiO@C-600-200-1-H₂O.

NMR and GCMS spectra

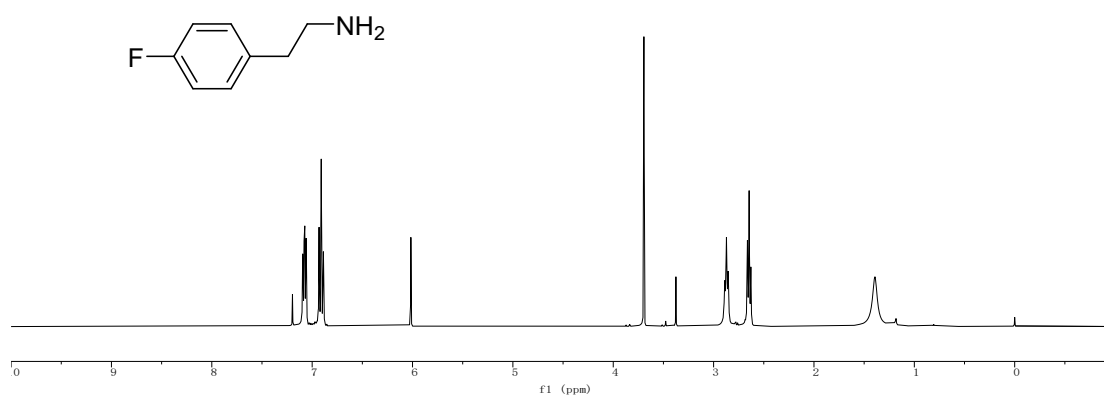
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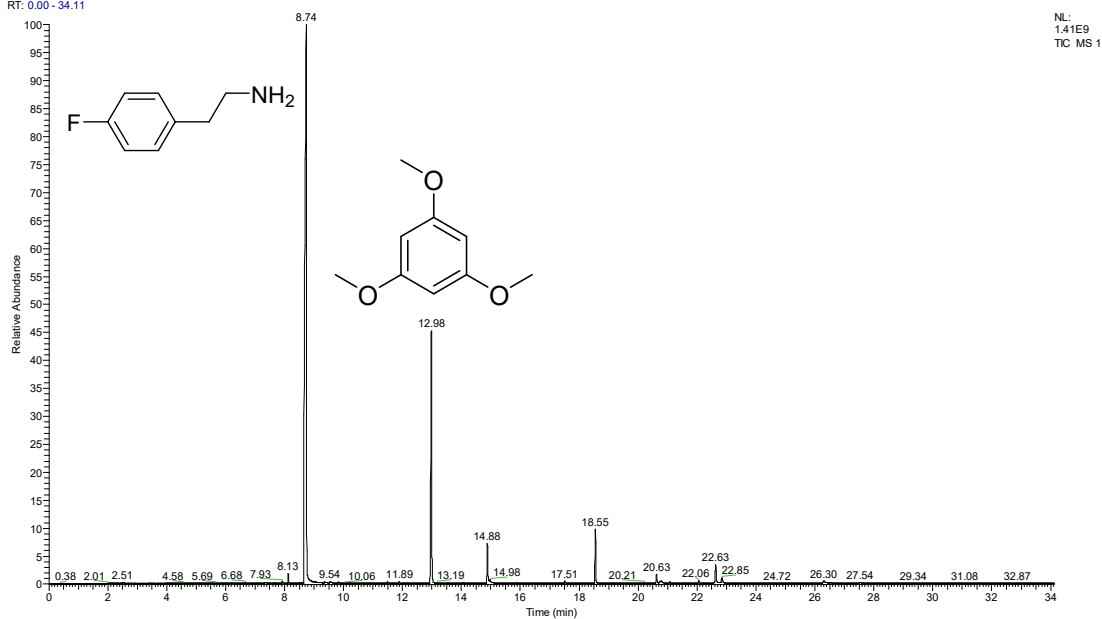
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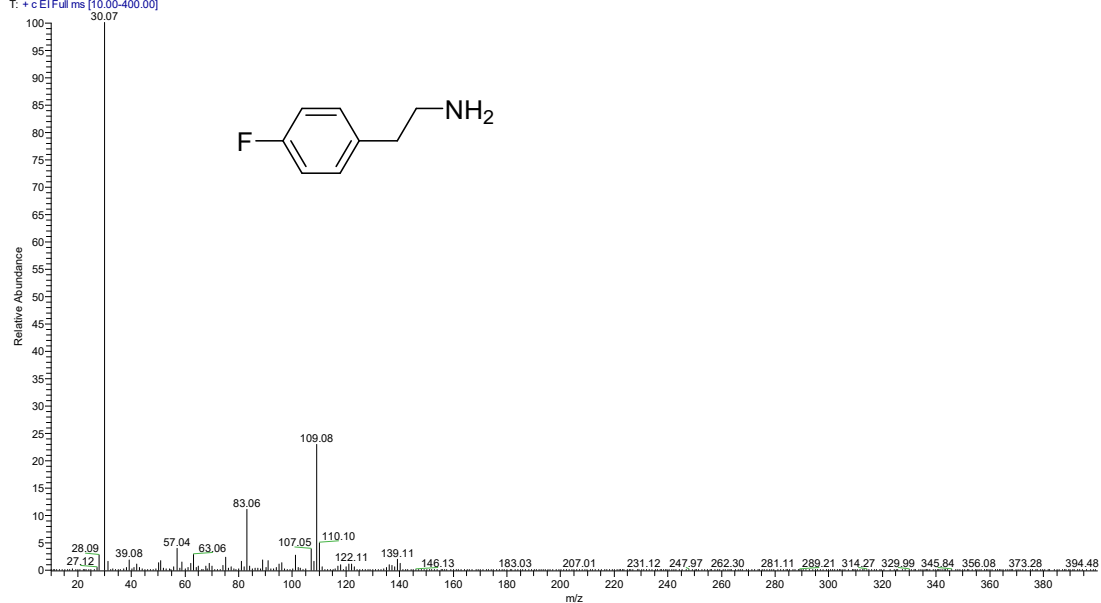
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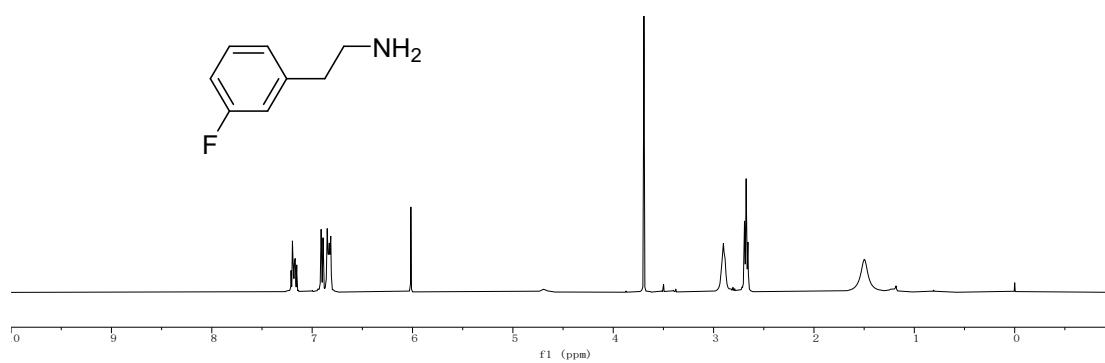
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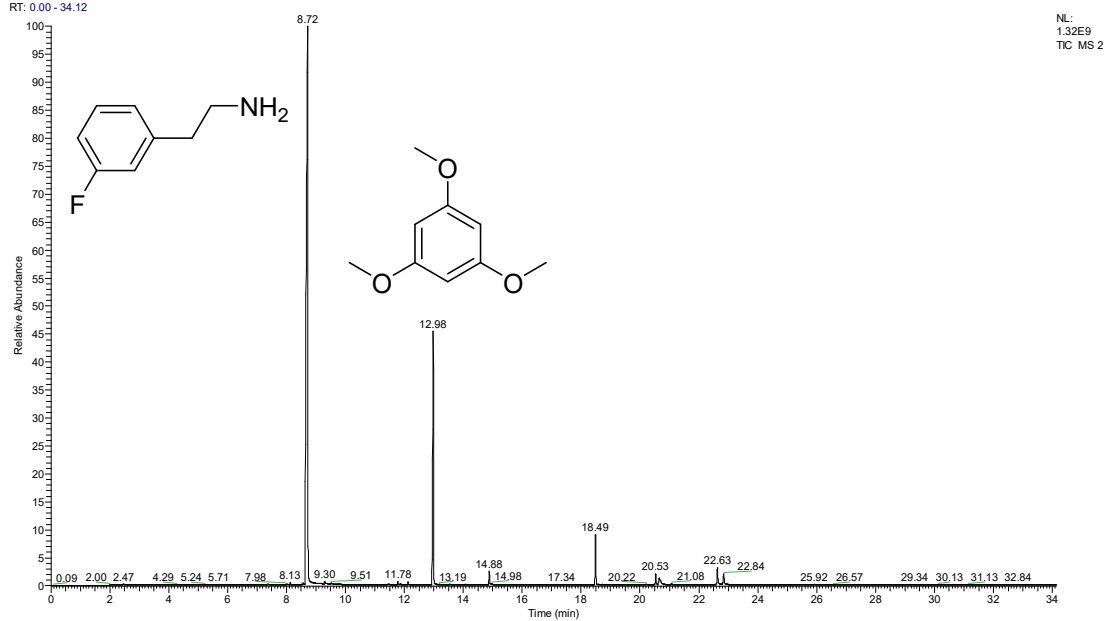
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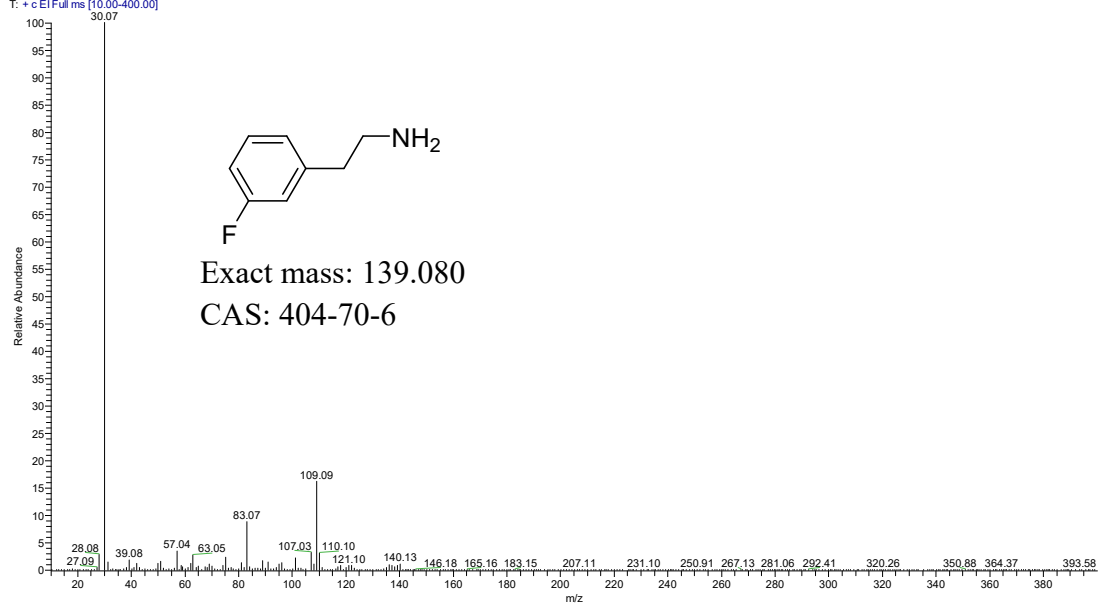
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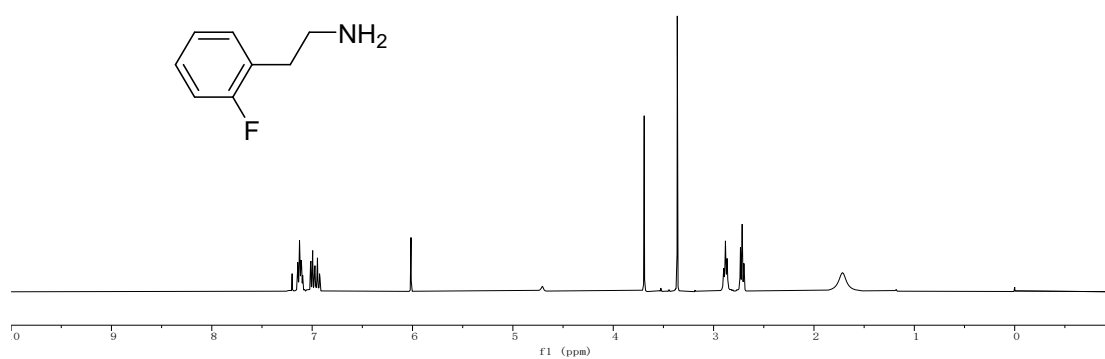
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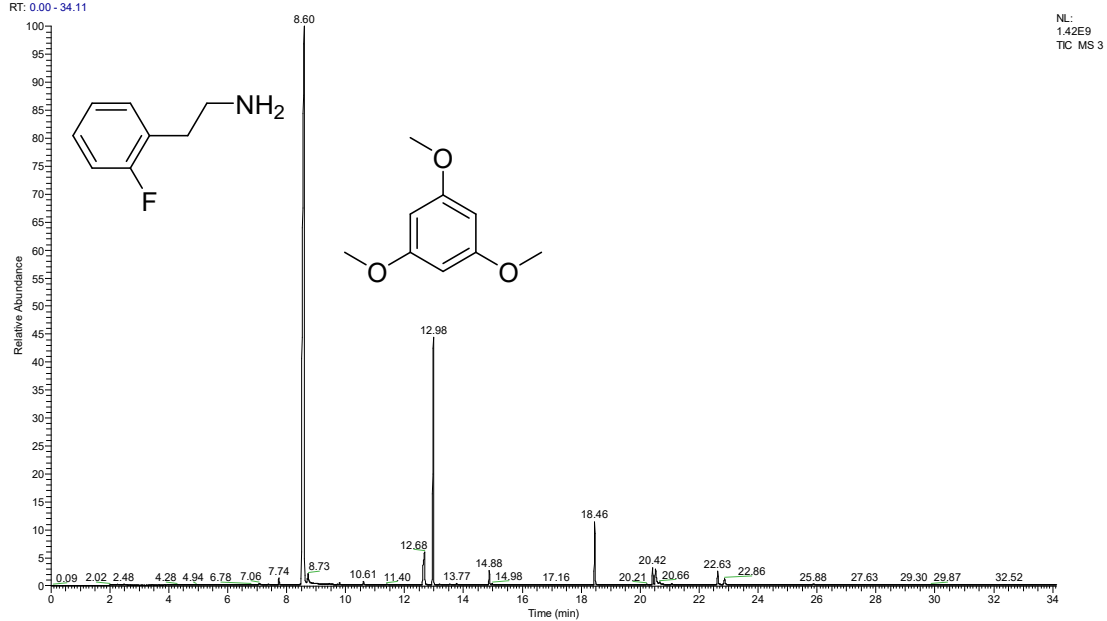
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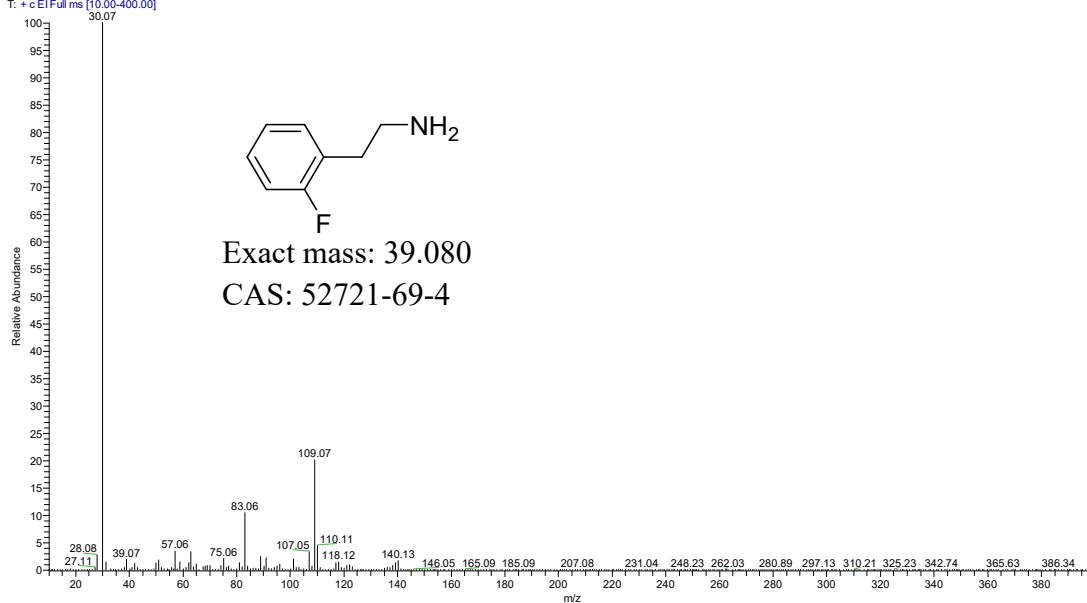
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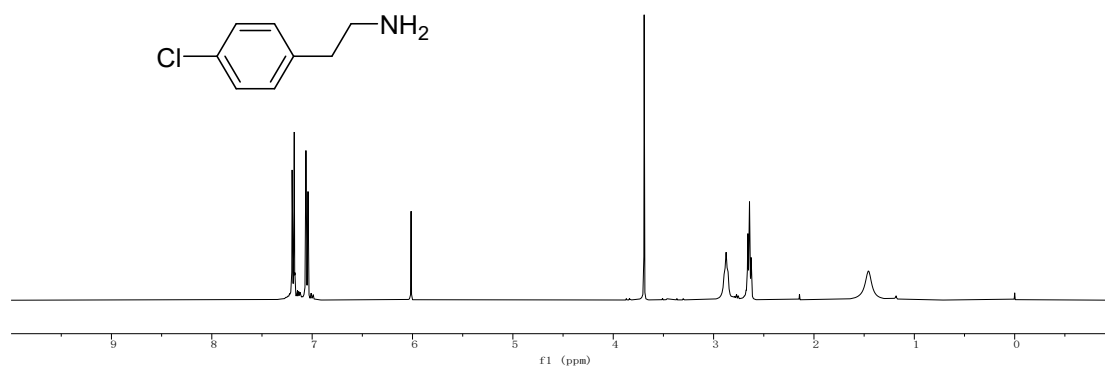
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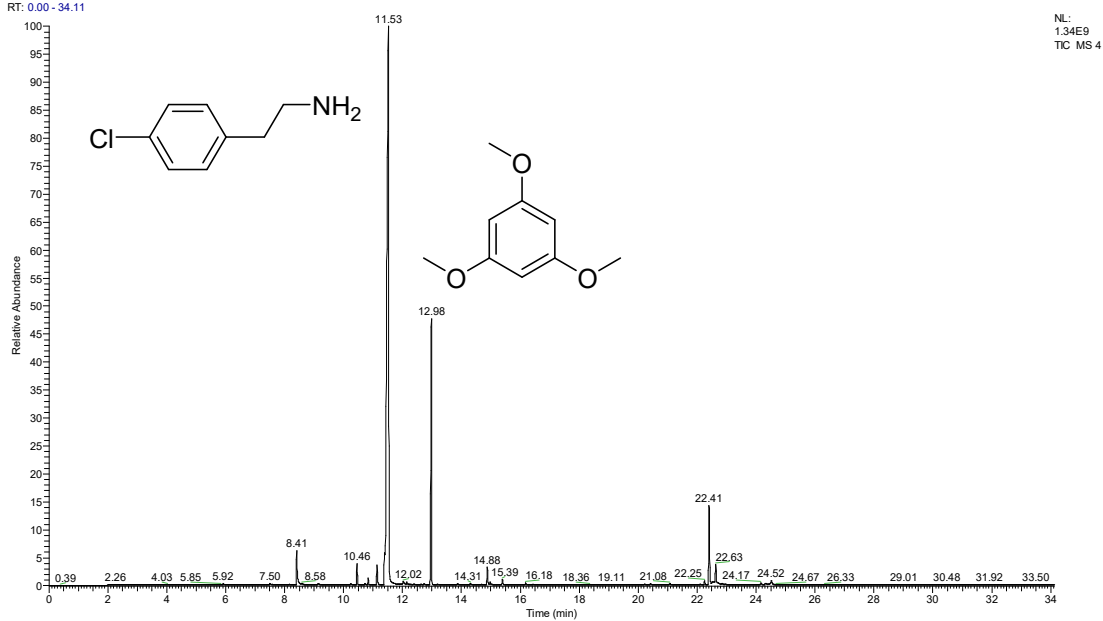
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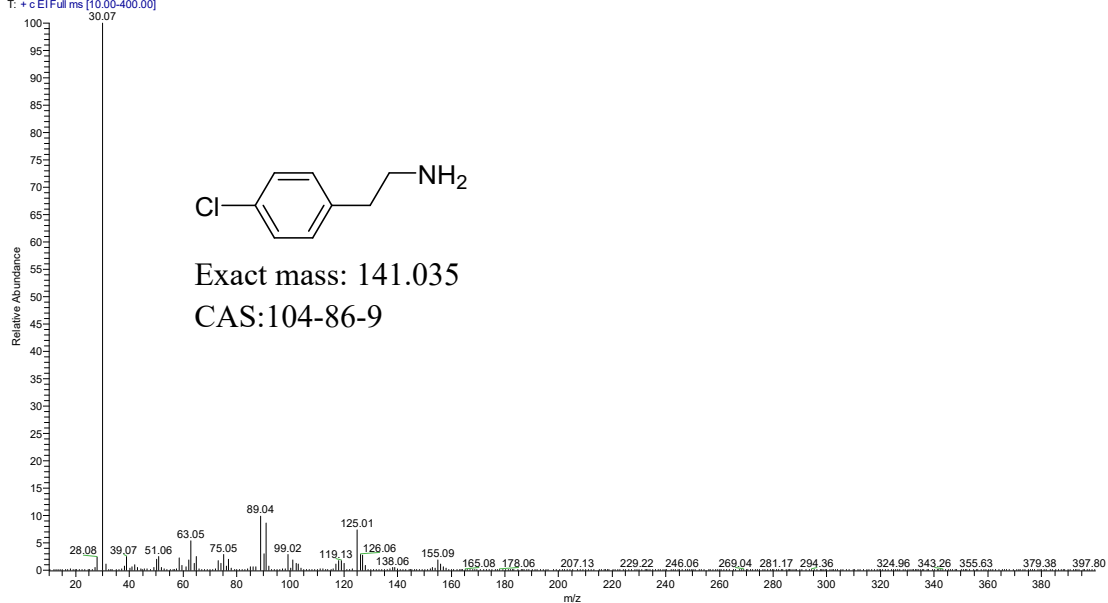
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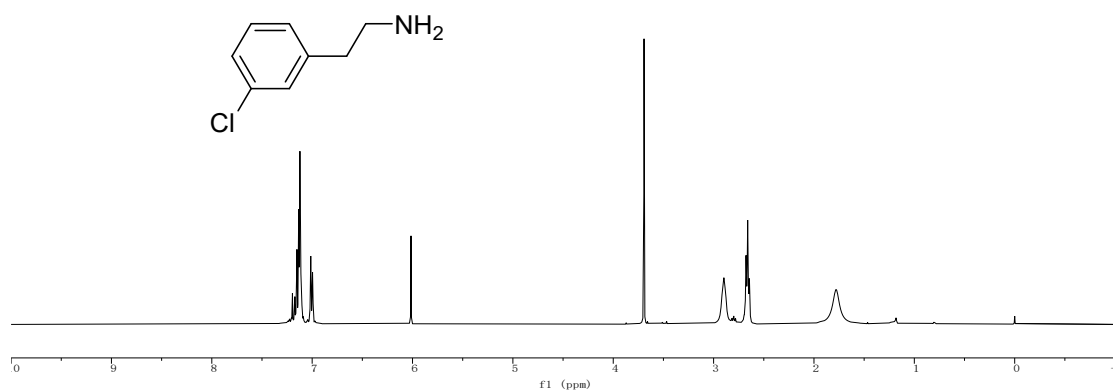
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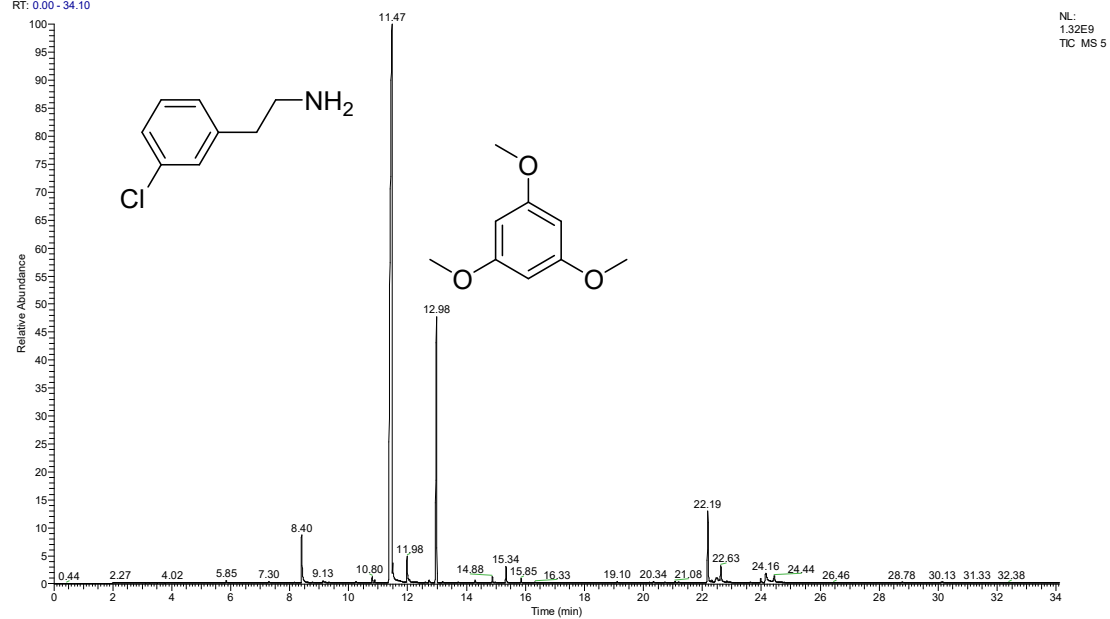
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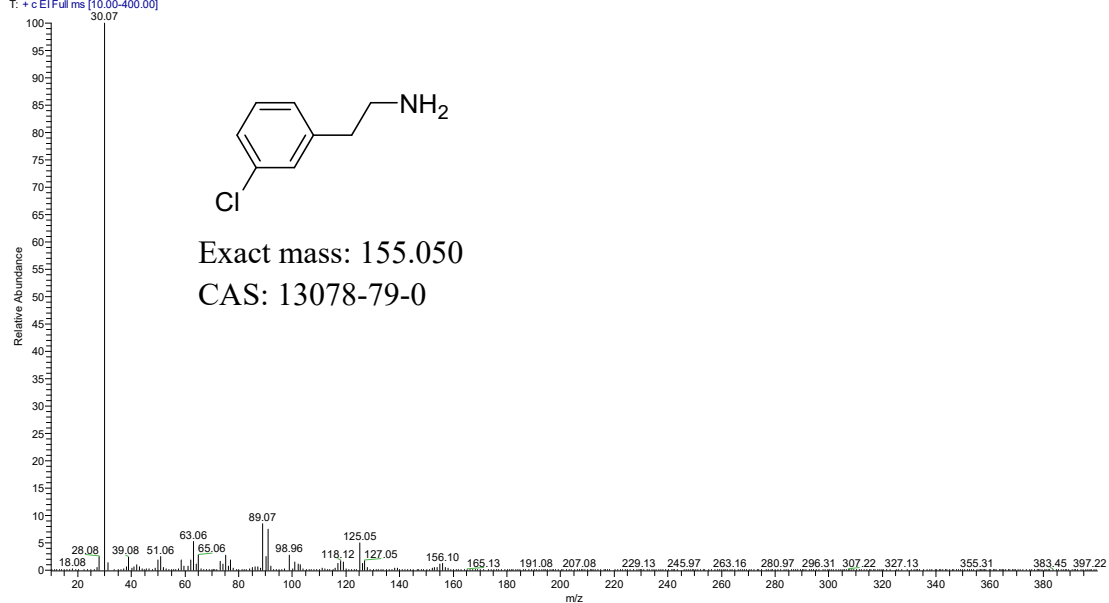
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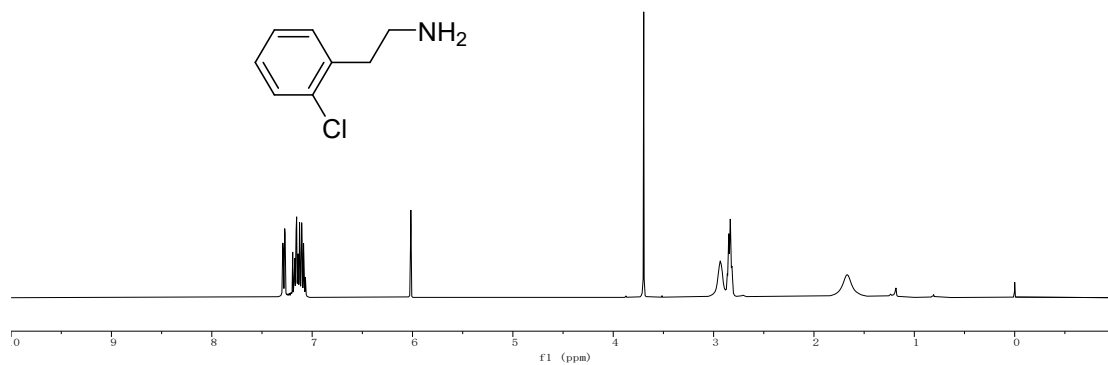
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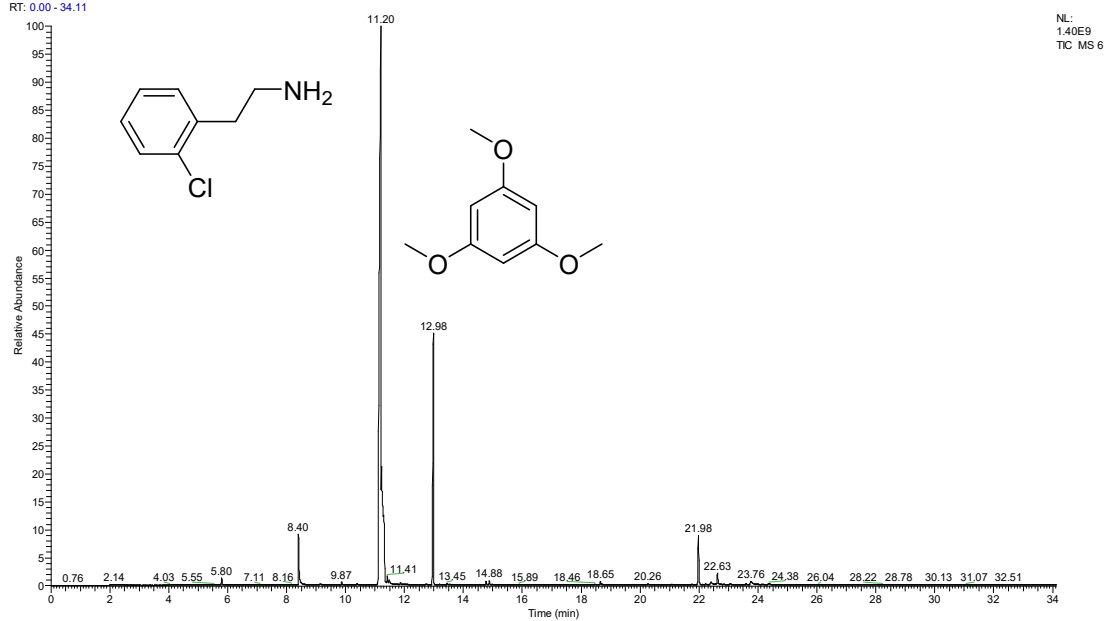
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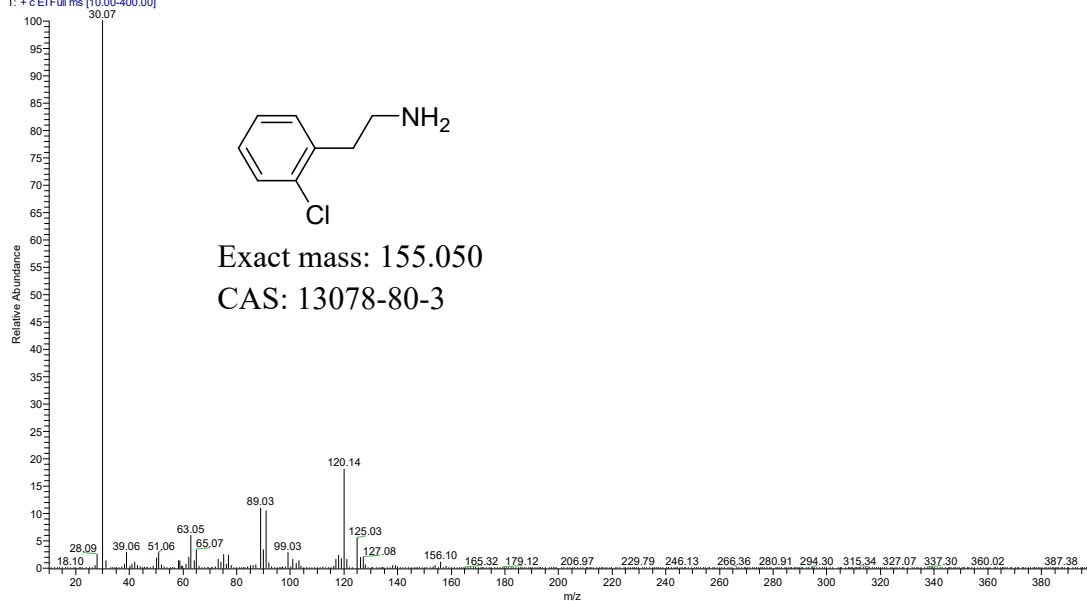
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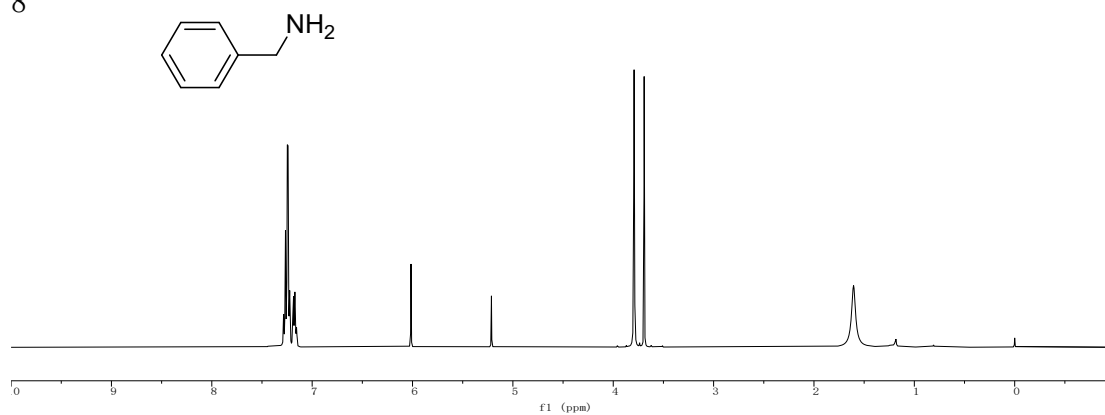
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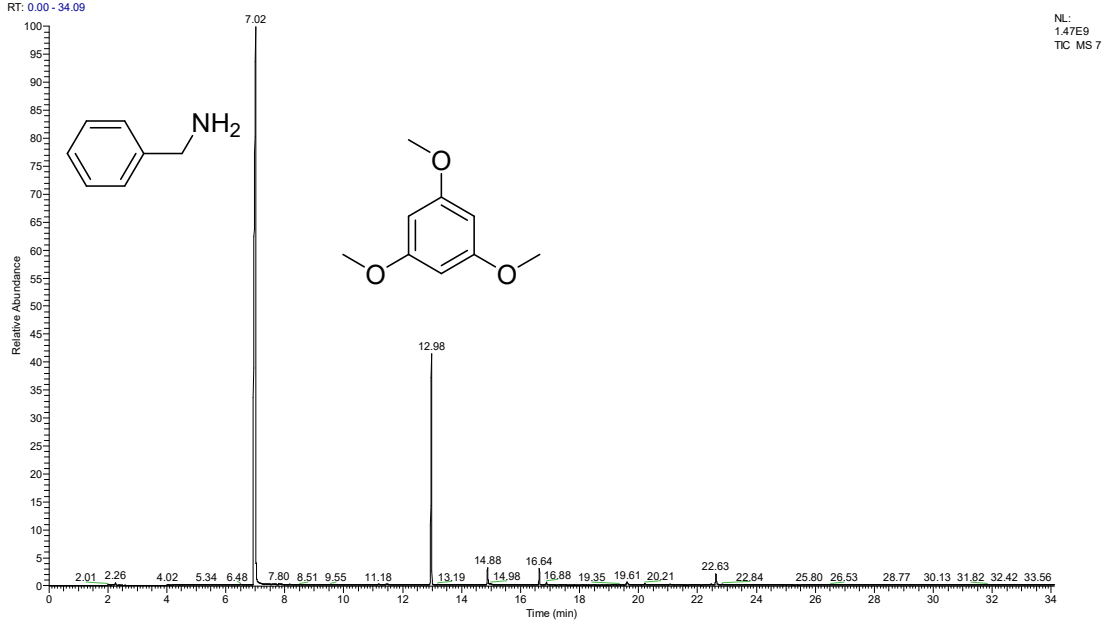
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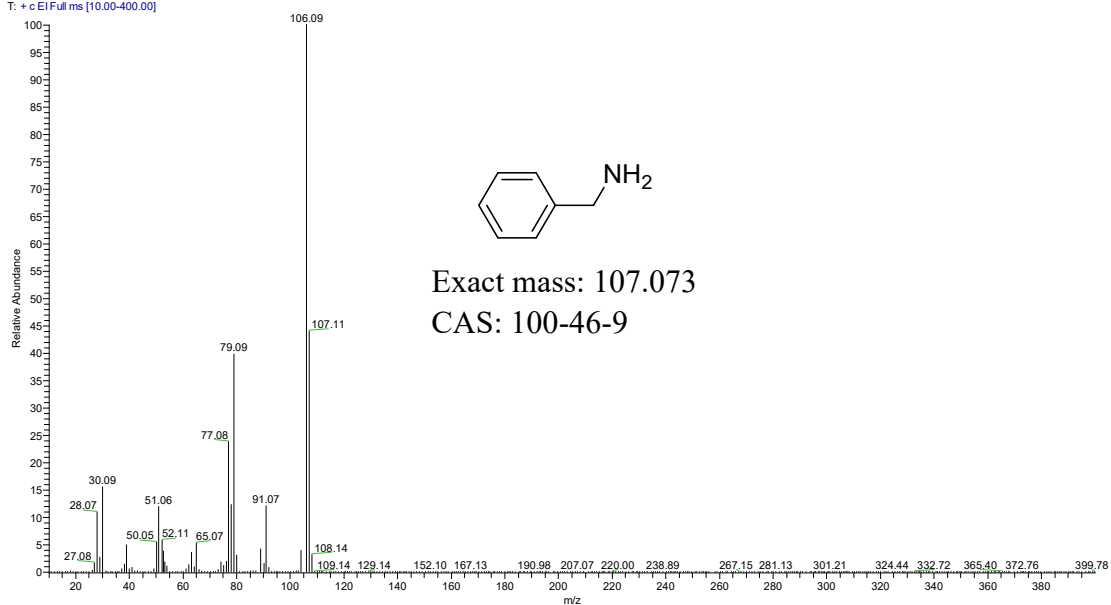
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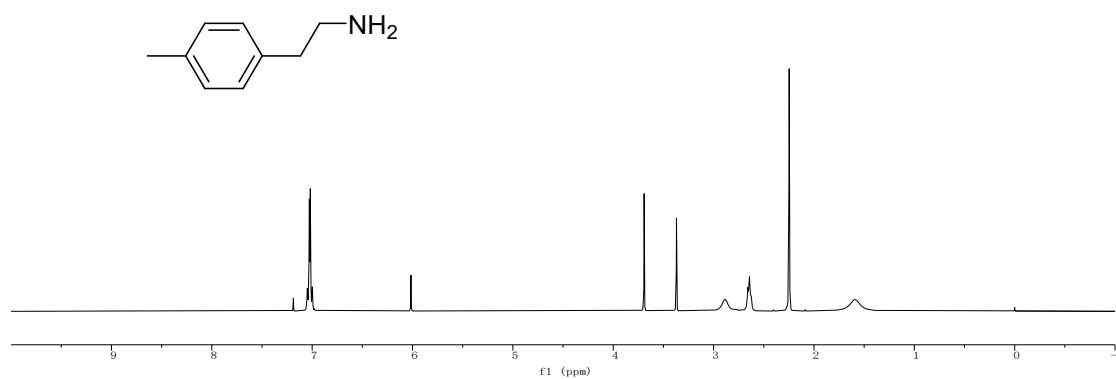
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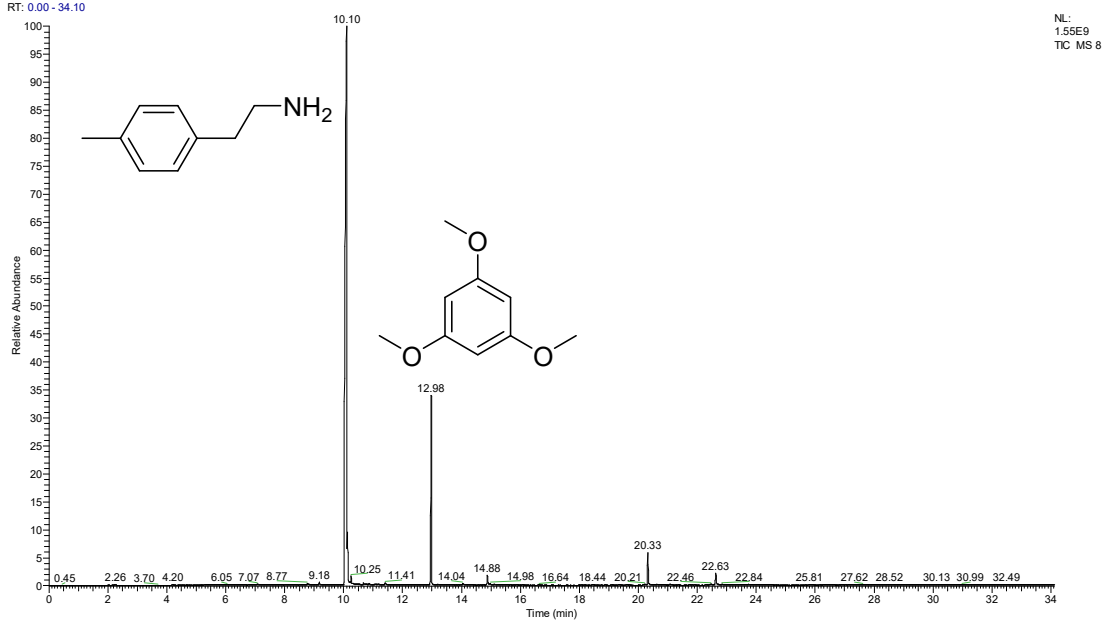
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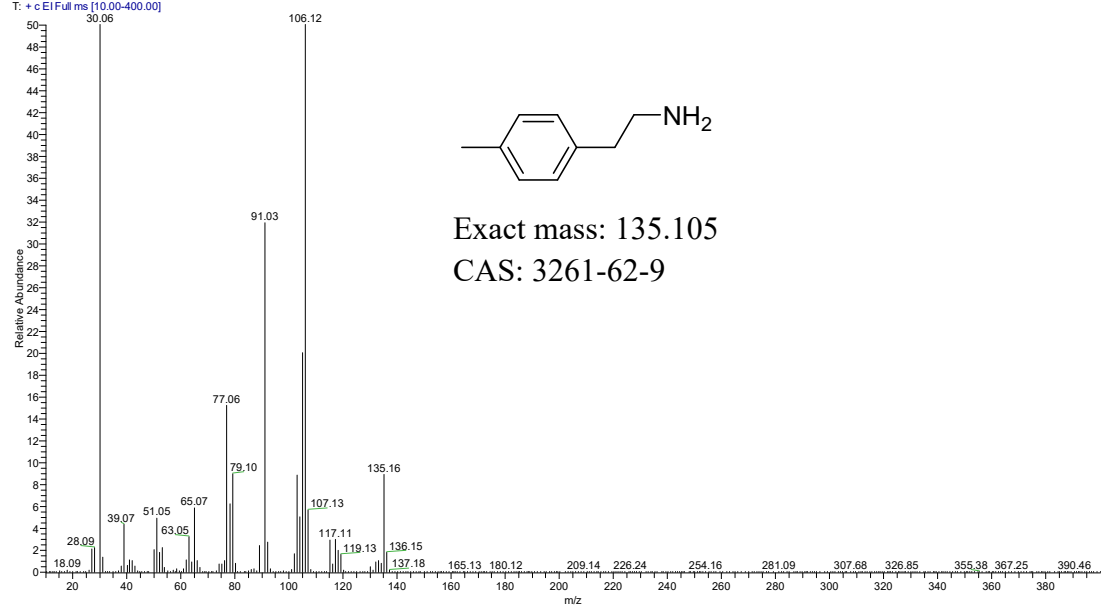
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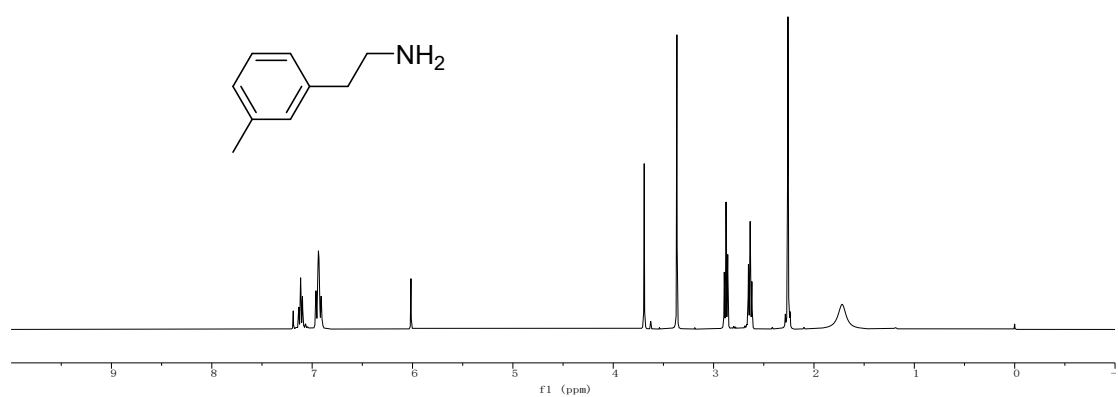
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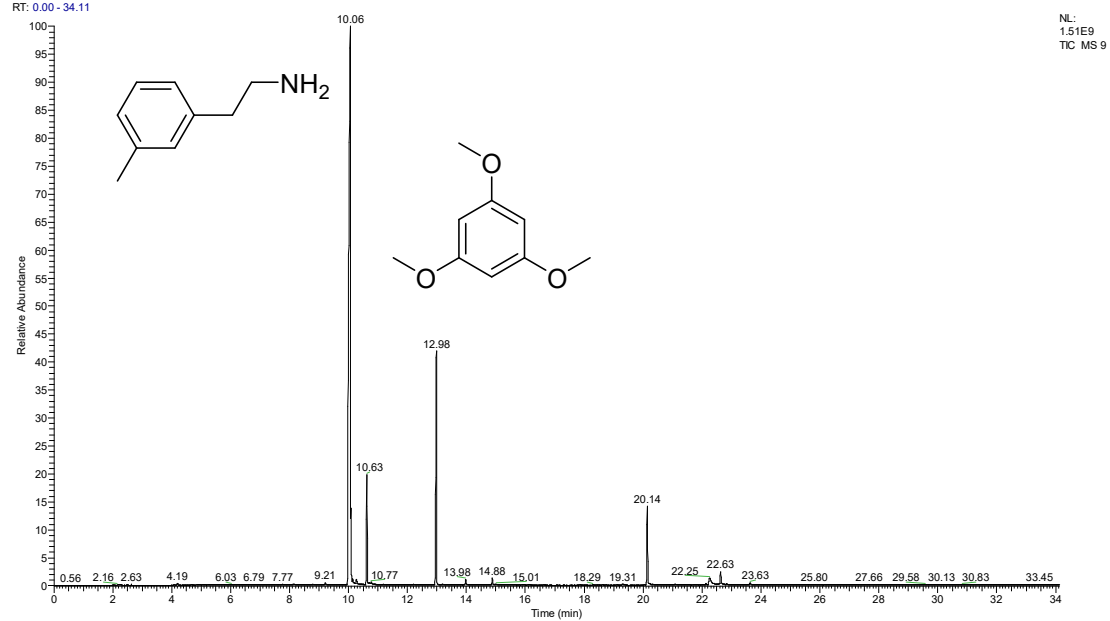
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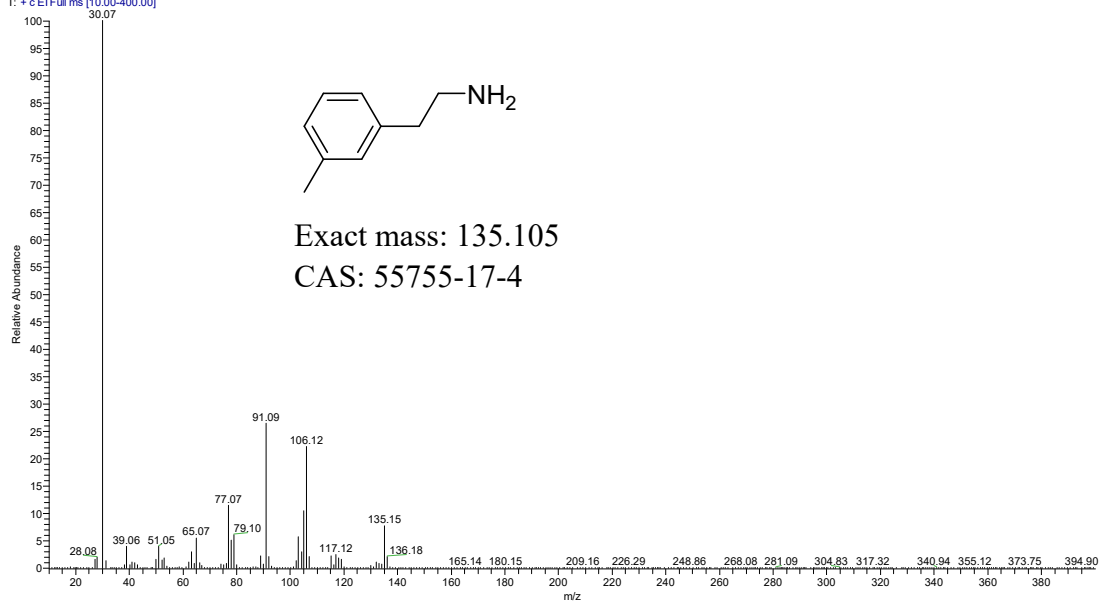
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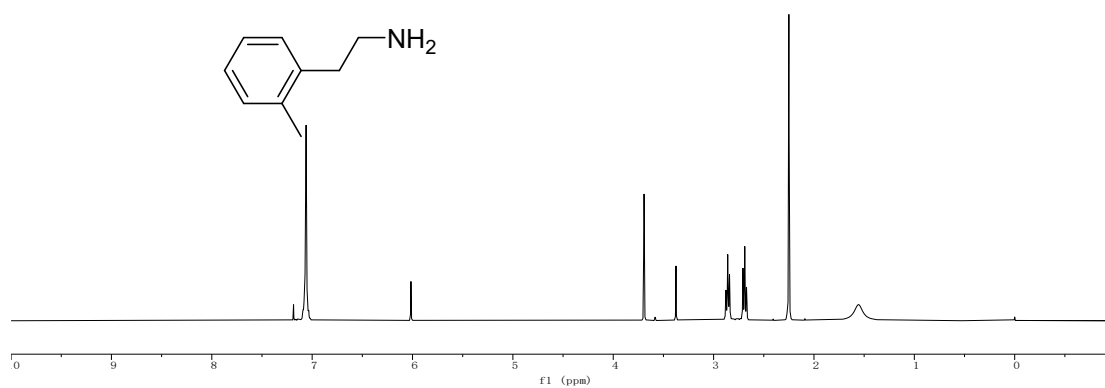
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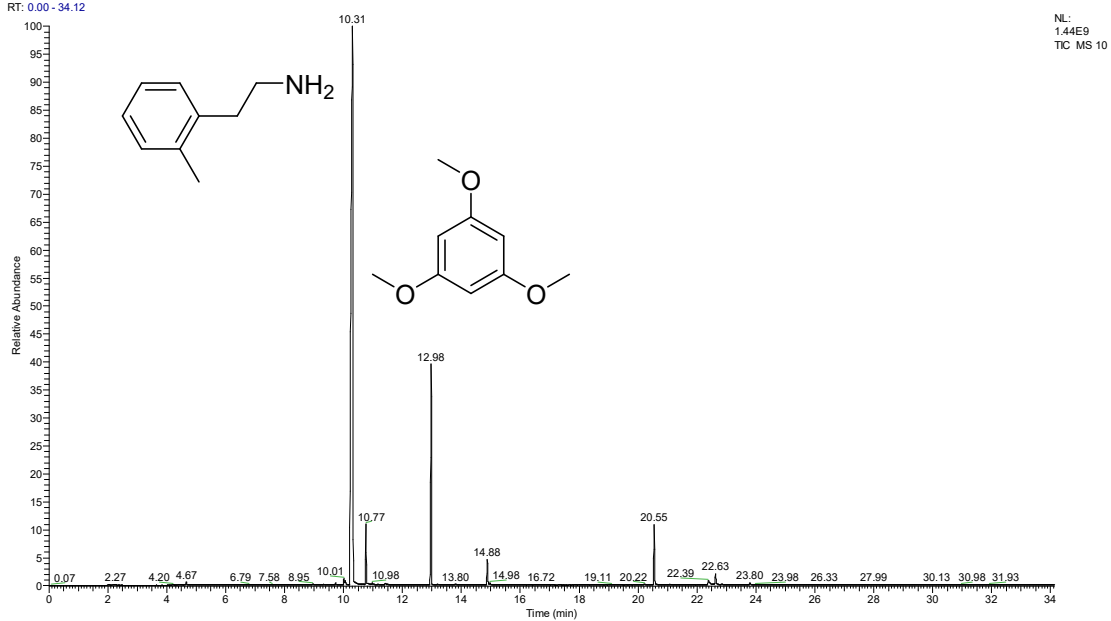
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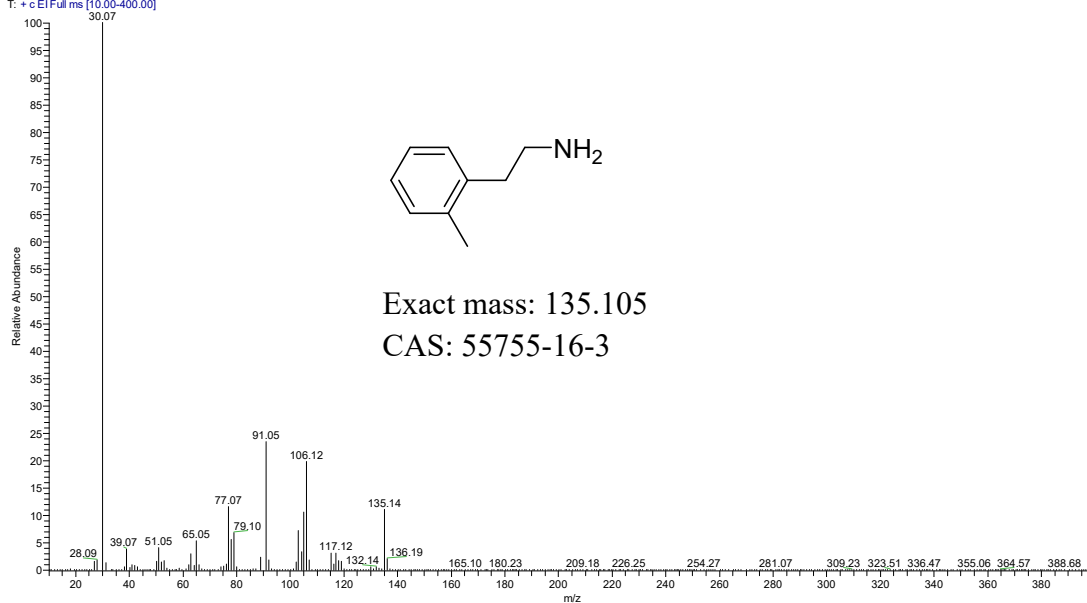
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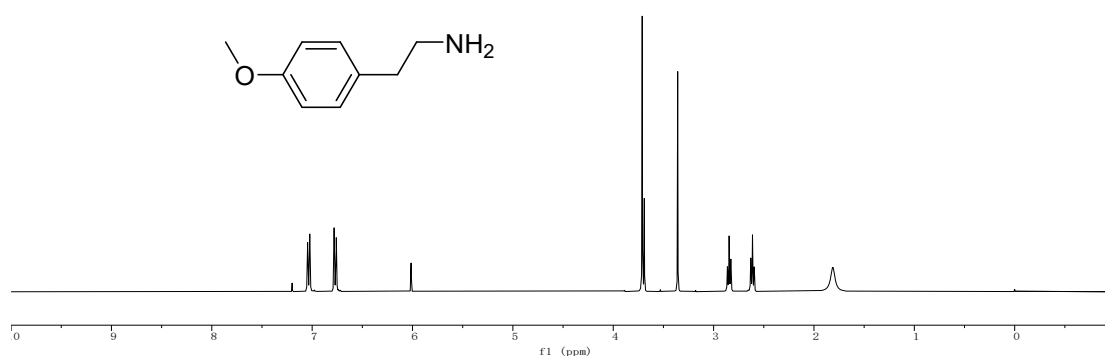
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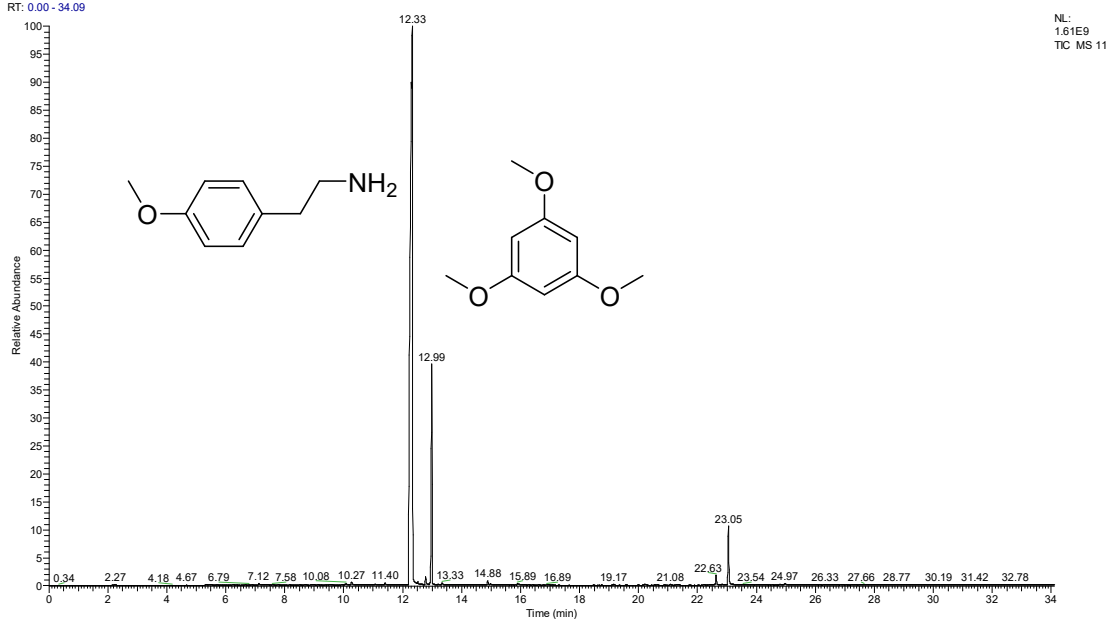
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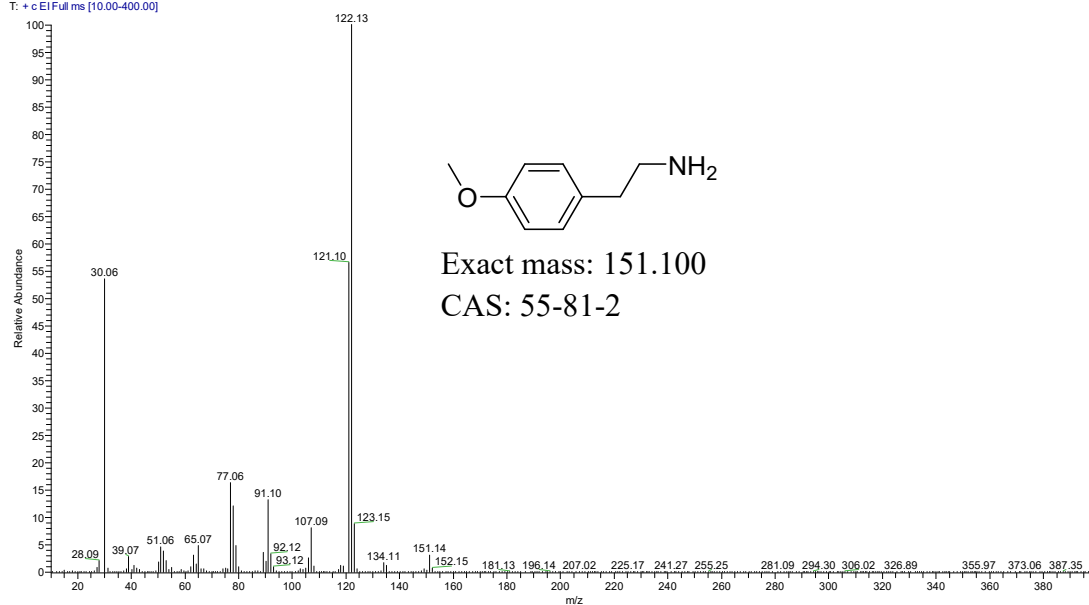
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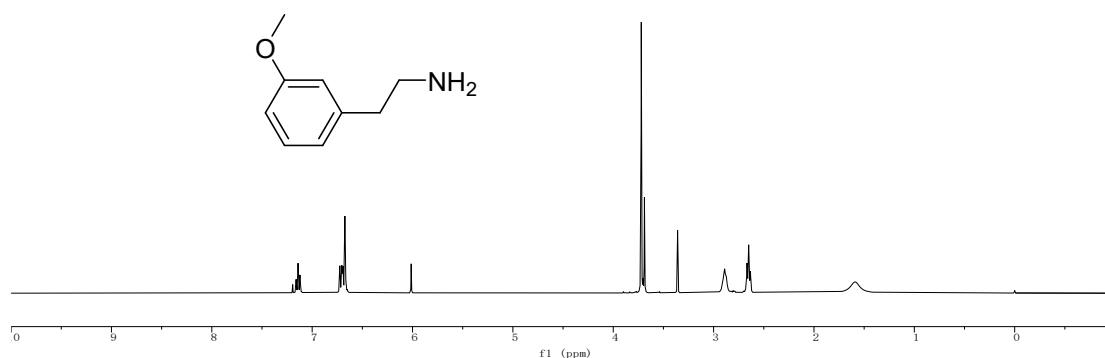
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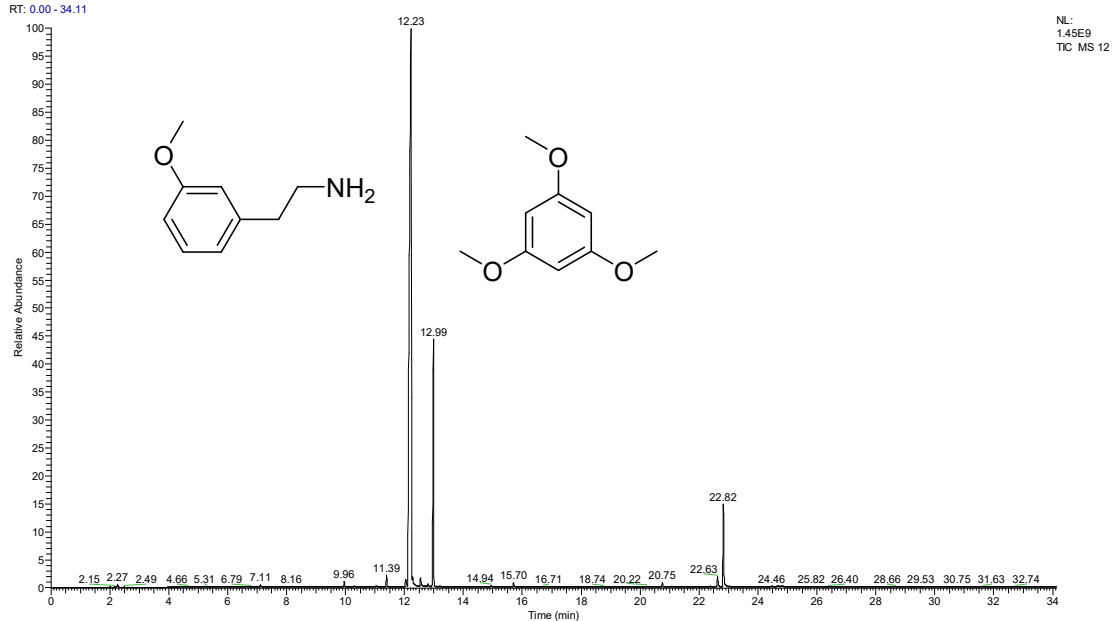
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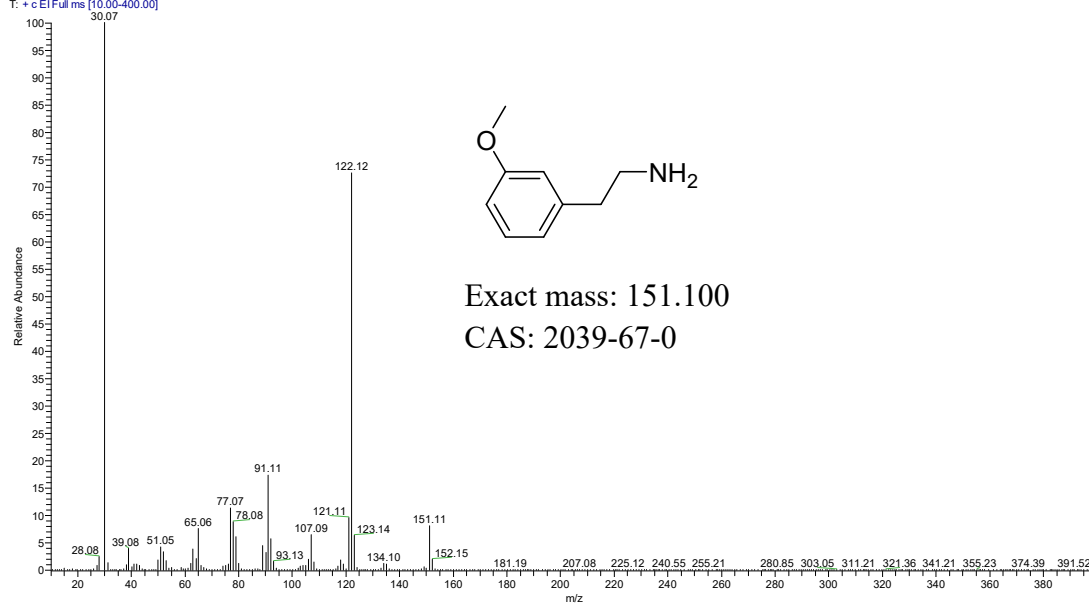
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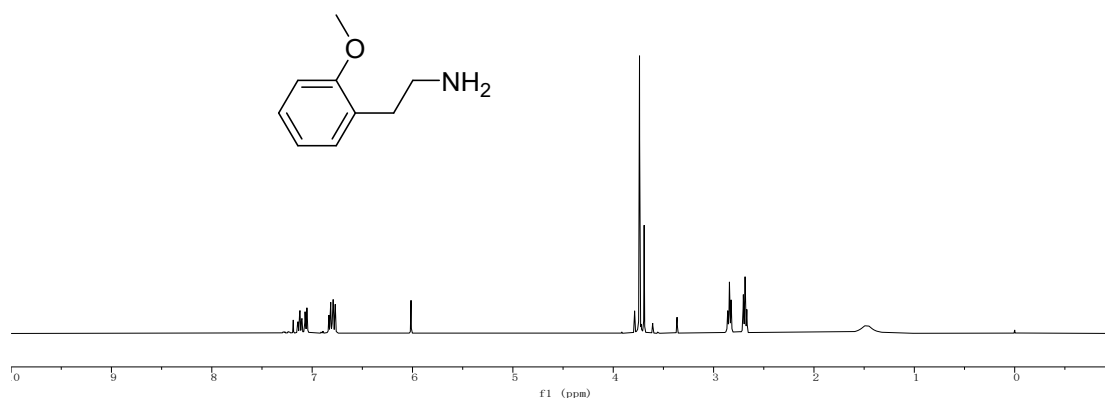
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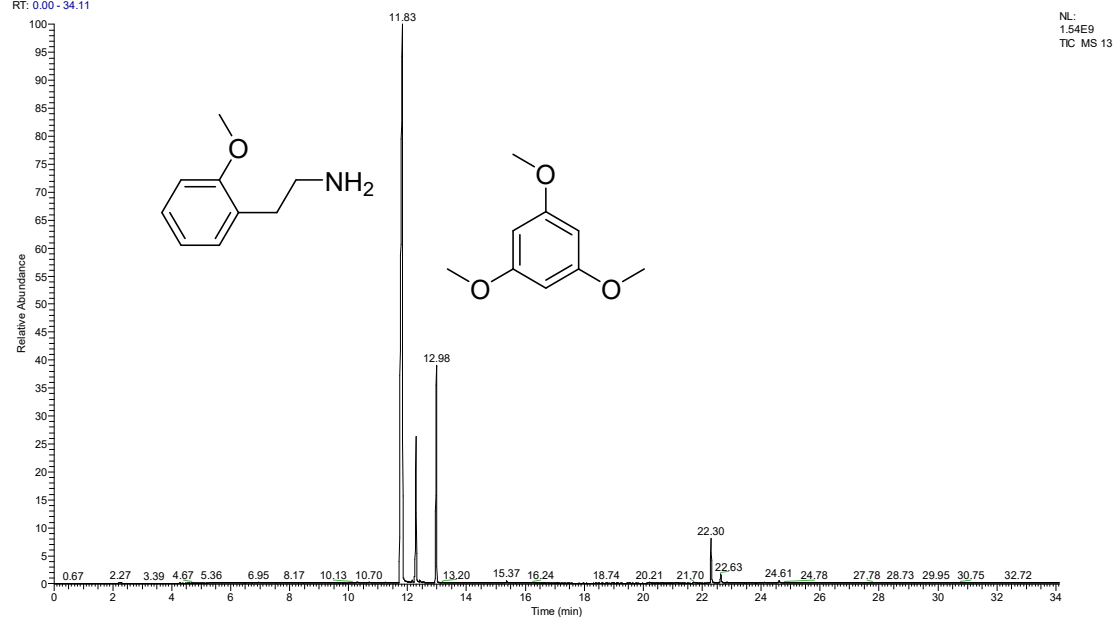
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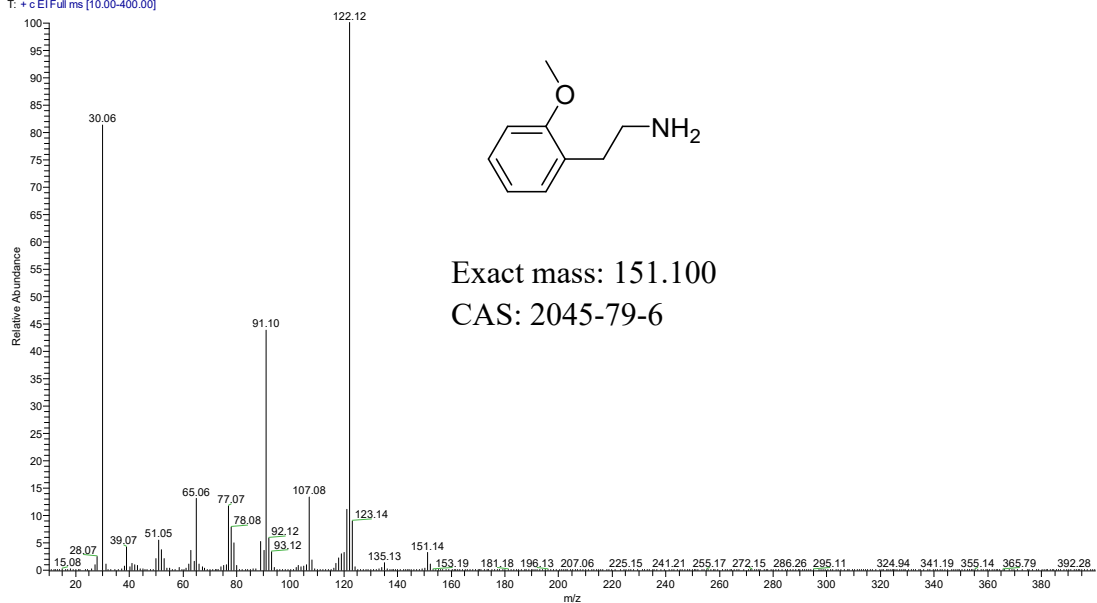
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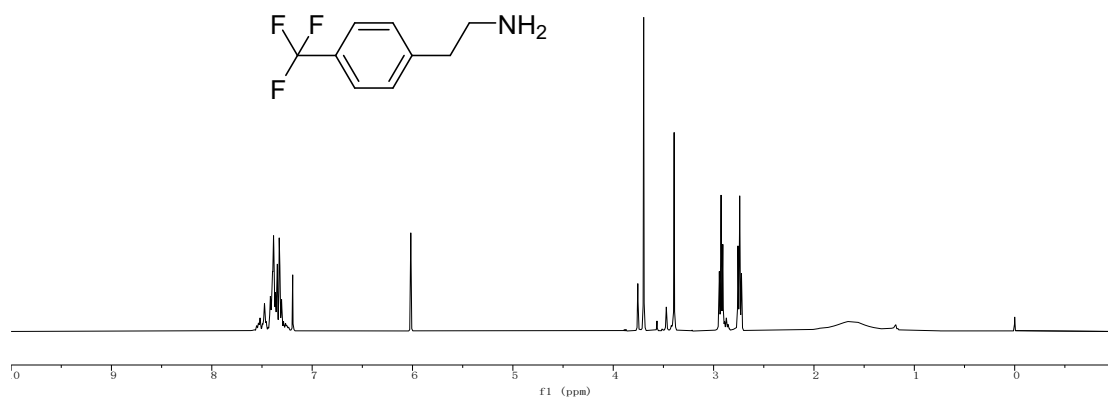
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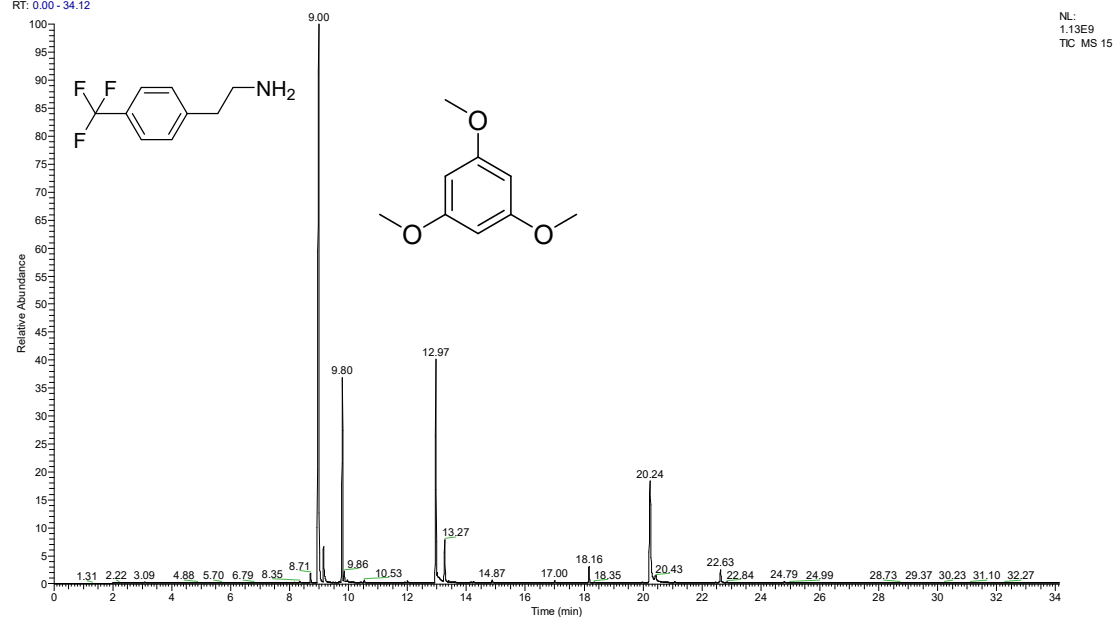
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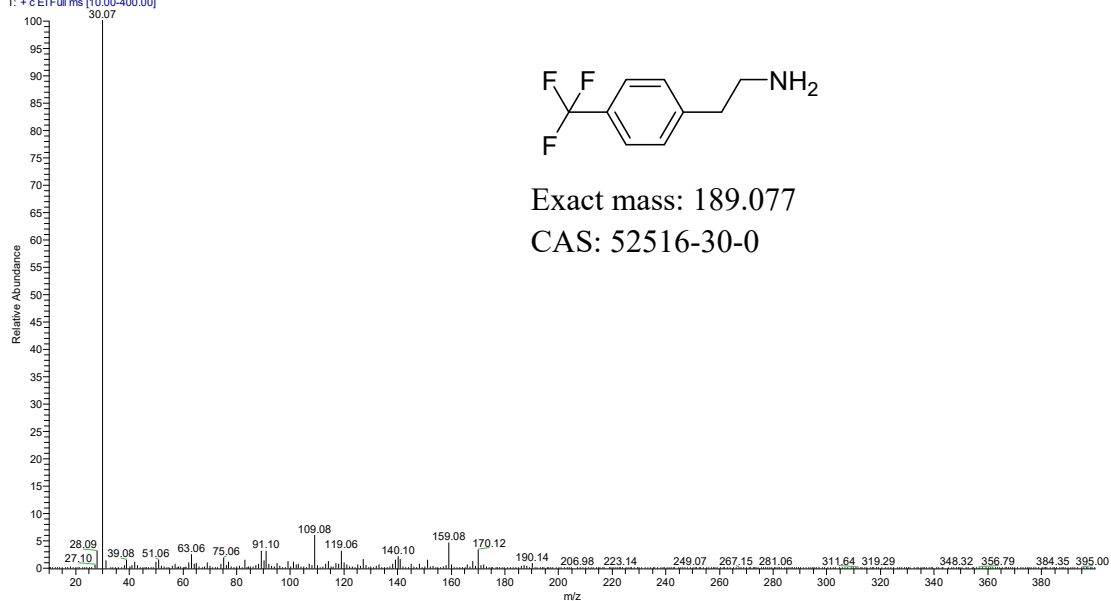
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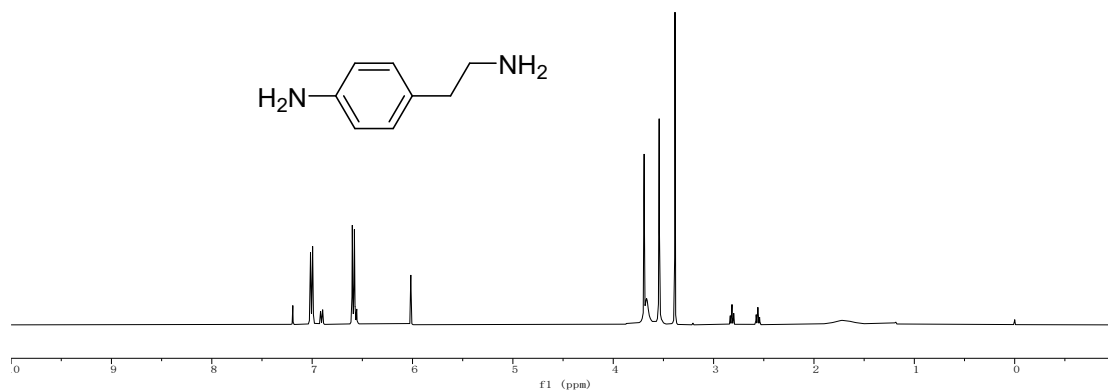
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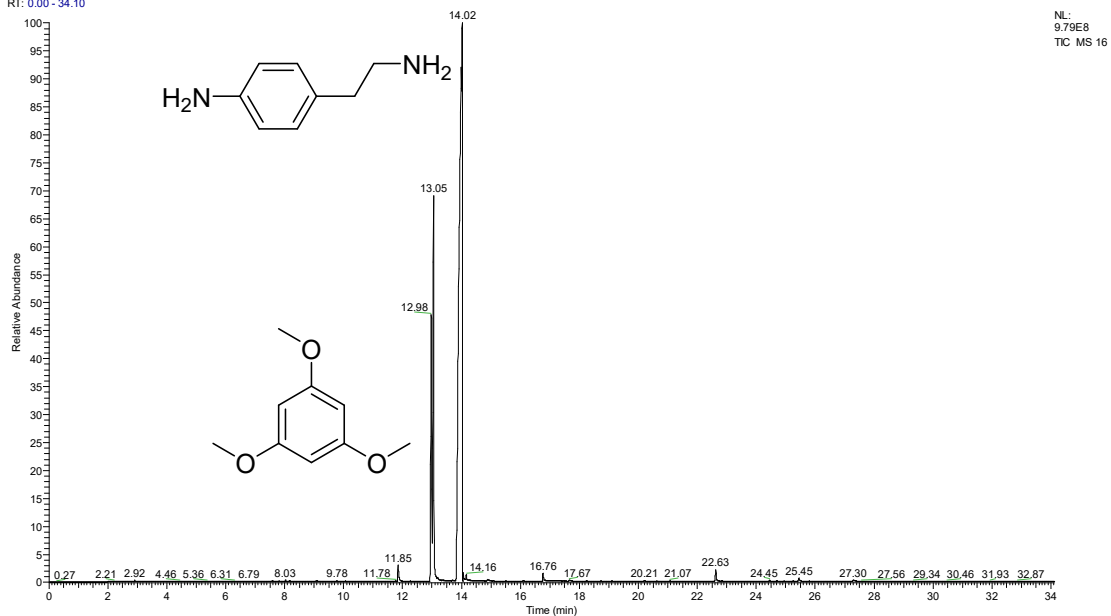
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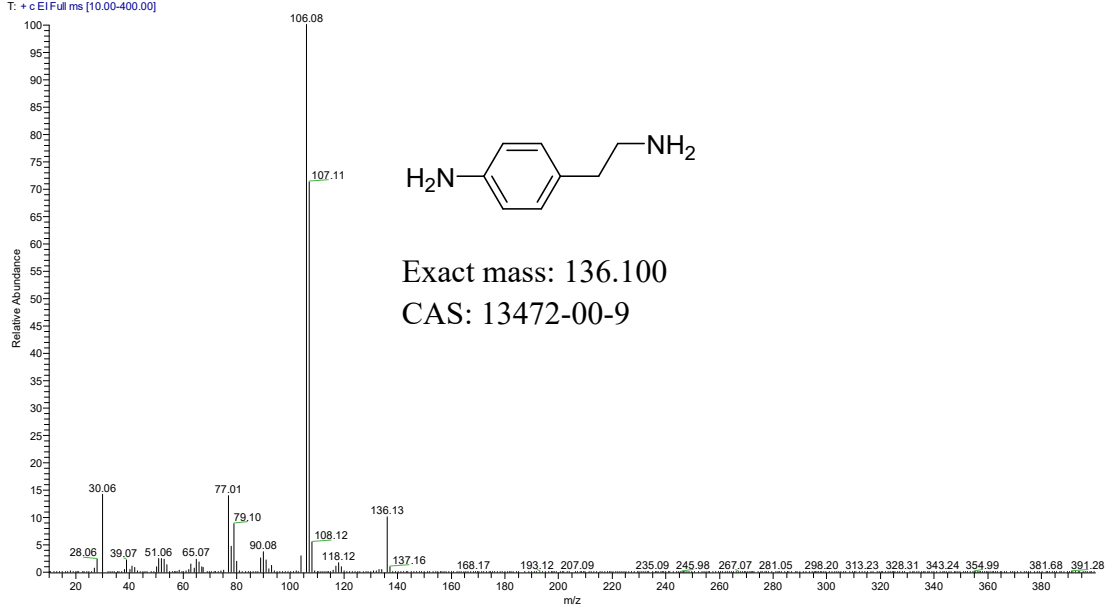
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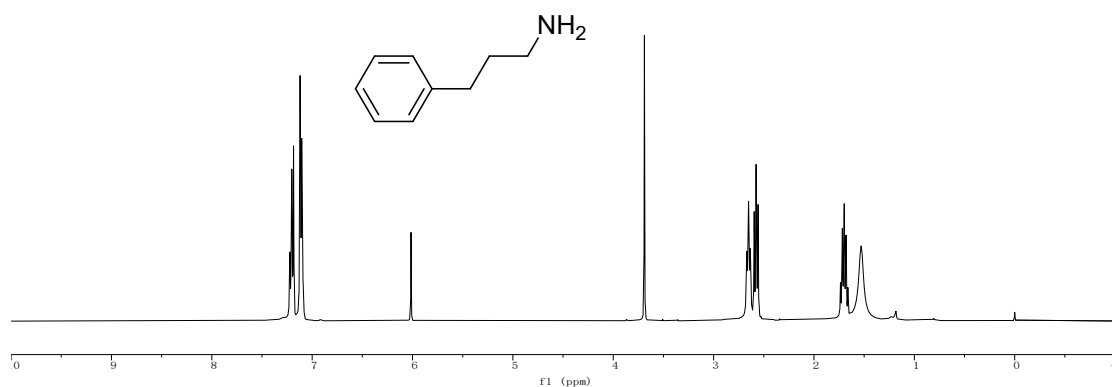
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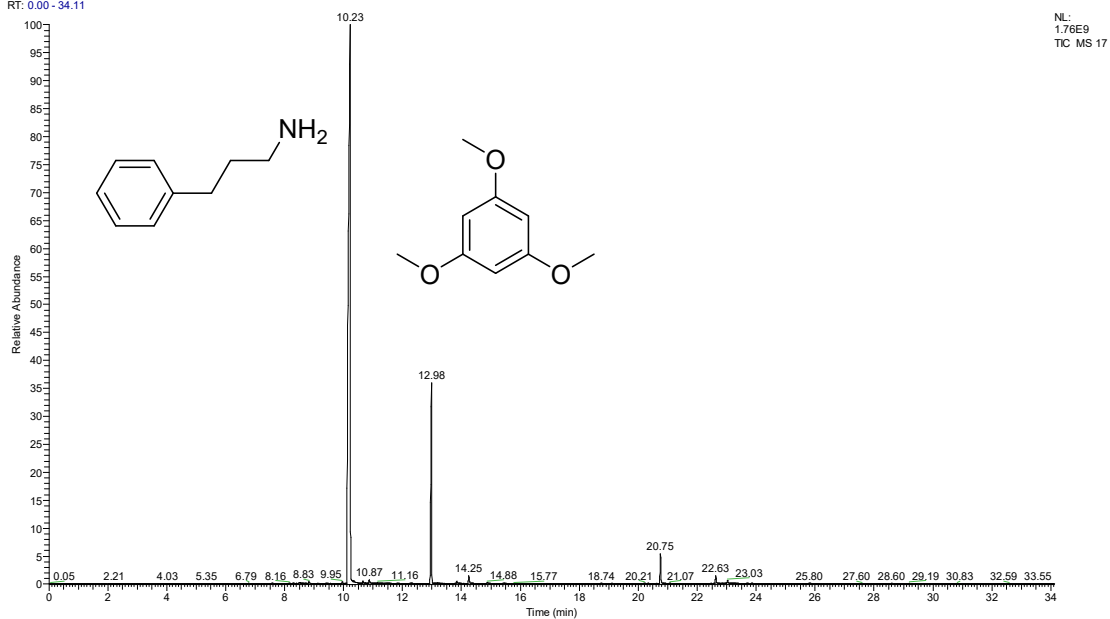
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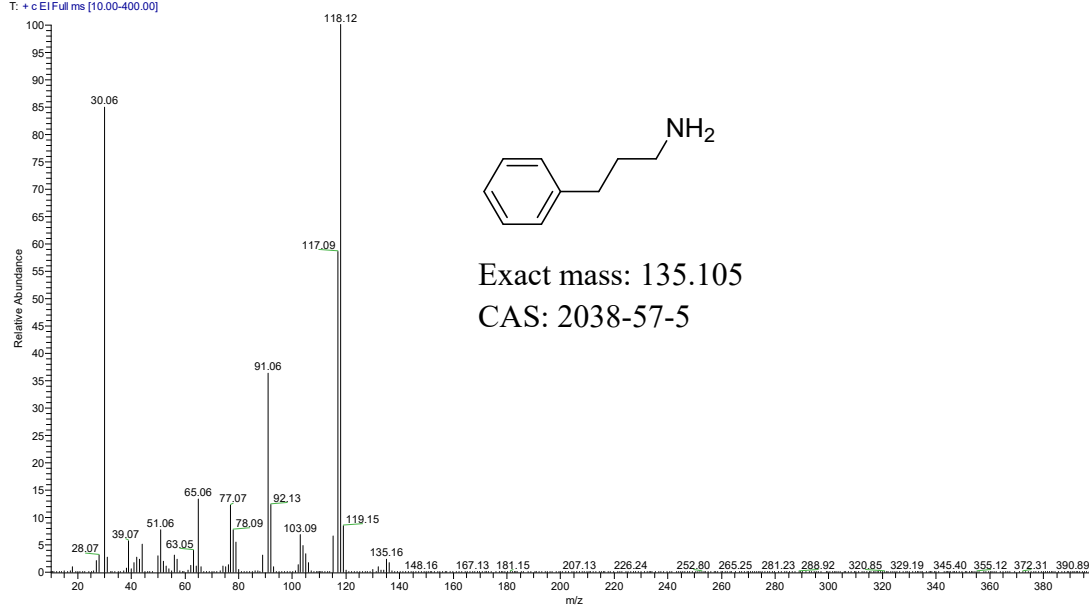
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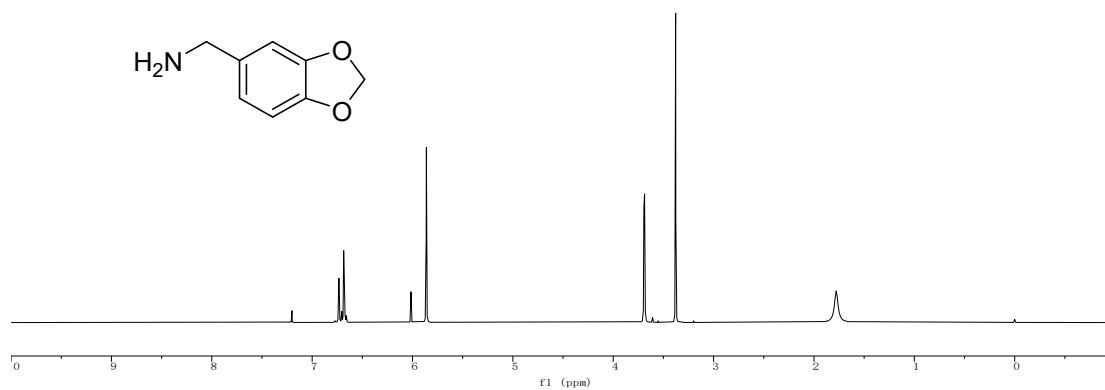
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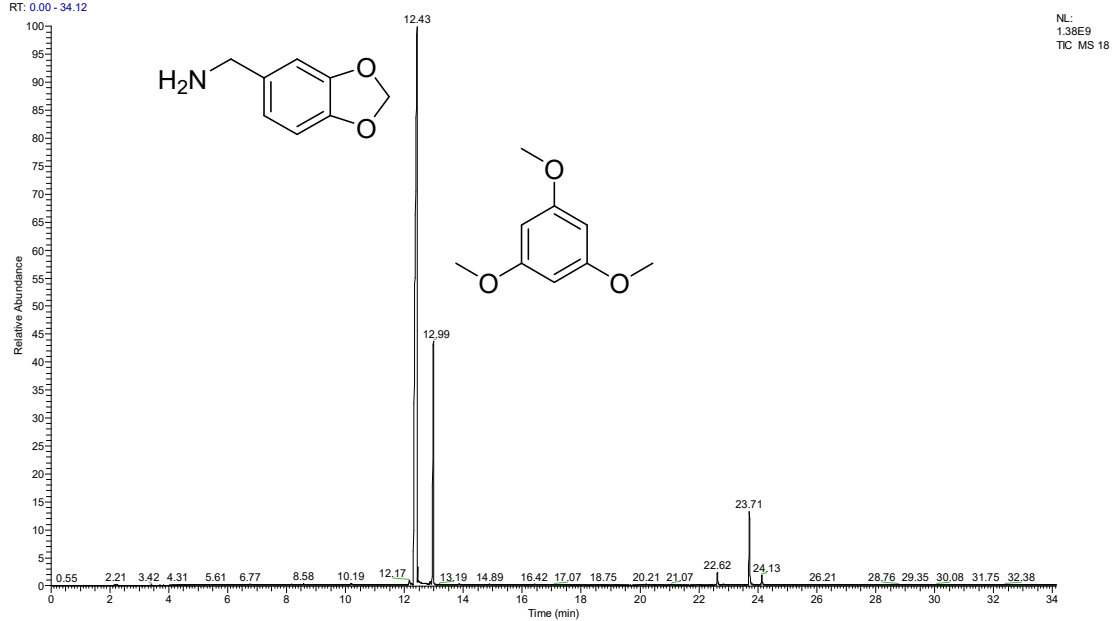
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18



RT: 0.00 - 34.12



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