BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Synthesis of *N*-phenyl- and *N*-thiazolyl-1*H*-indazoles by copper-catalyzed intramolecular *N*-arylation of *ortho*-chlorinated arylhydrazones

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Reaction analysis by ^{1}H and ^{13}C NMR spectroscopy, characterization data, NMR spectra for the 1*H*-indazoles and HRMS spectra for the arylhydrazones and 1*H*-indazoles

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Reaction analysis by ^{1}H and ^{13}C NMR

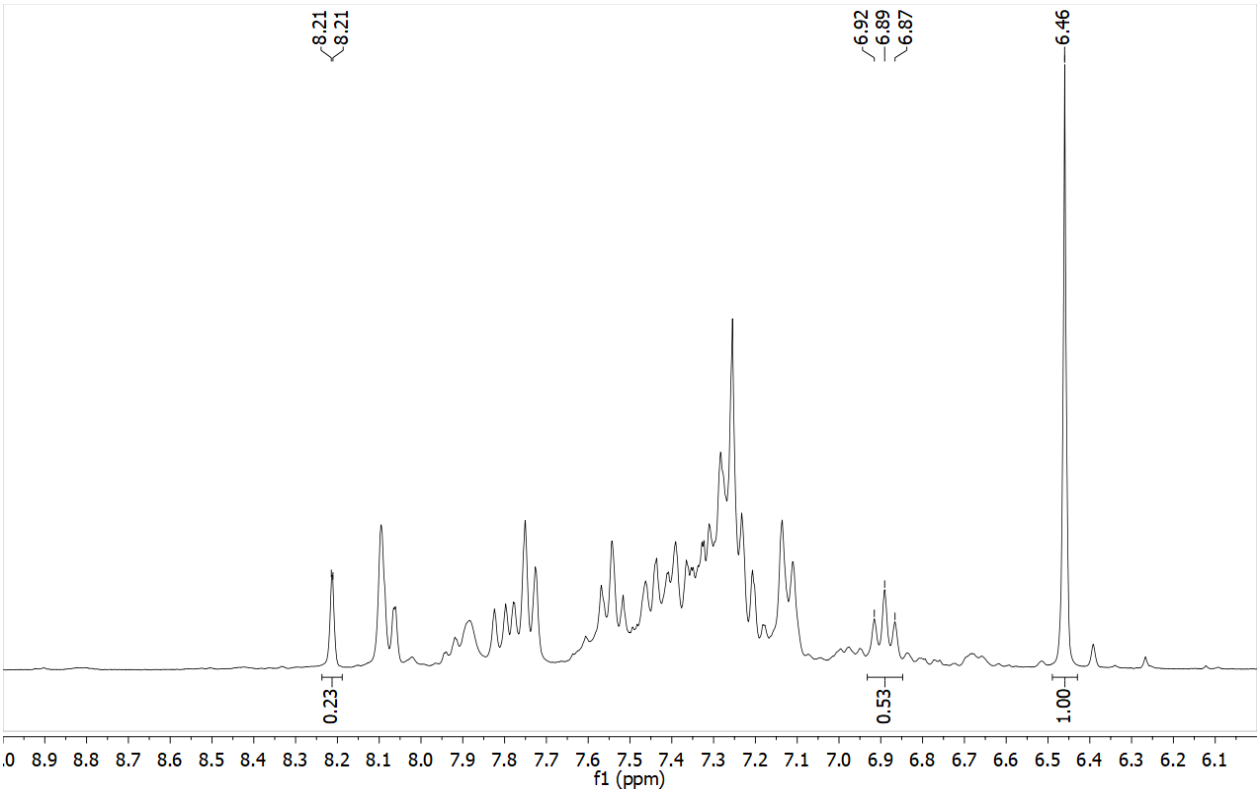


Figure S1. ^{1}H NMR spectrum of the crude product of the reaction of **1a** carried out at 100 °C + trichloroethylene (TCE, 300 MHz, $CDCl_3$).

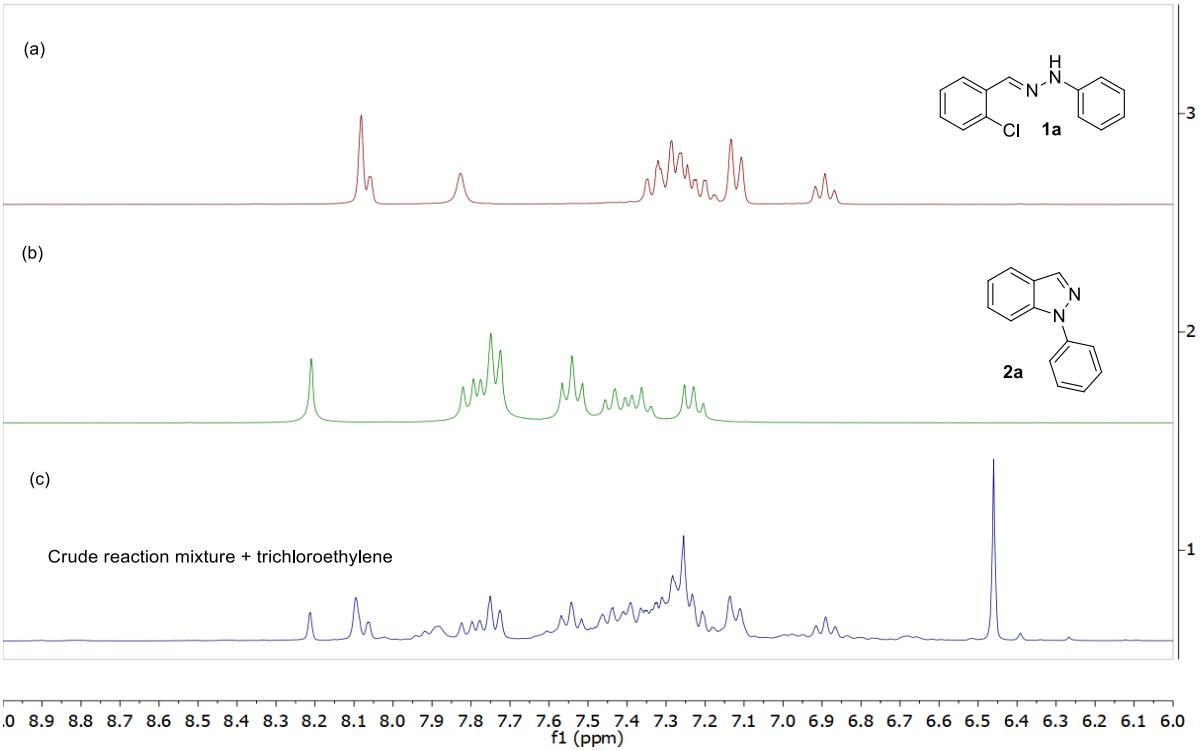


Figure S2. ^{1}H NMR spectra of (a) **1a** (300 MHz, $CDCl_3$), (b) **2a** (300 MHz, $CDCl_3$), and (c) TCE + the crude product of the reaction of **1a** carried out at 100 °C (300 MHz, $CDCl_3$).

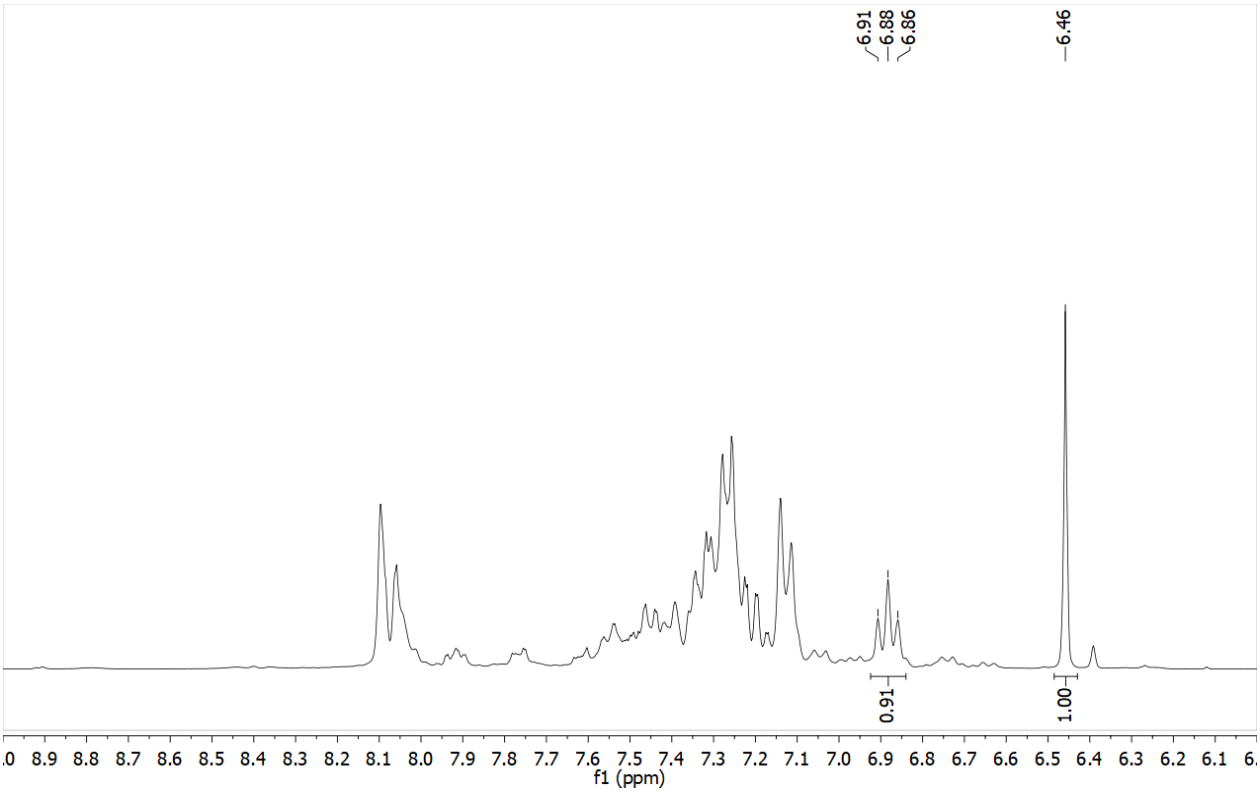


Figure S3. ^{1}H NMR spectrum of the crude product of the reaction of **1a** carried out in NMP + TCE (300 MHz, $CDCl_3$).

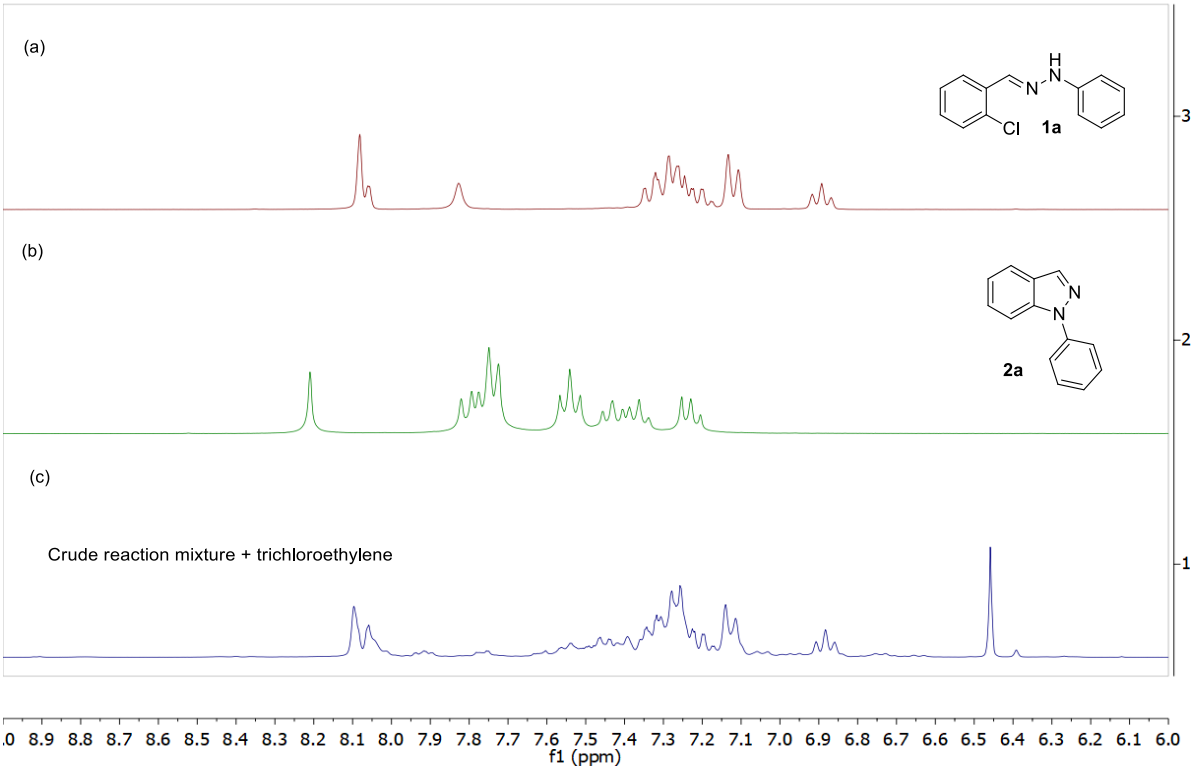


Figure S4. ^{1}H NMR spectra of (a) **1a** (300 MHz, $CDCl_3$), (b) **2a** (300 MHz, $CDCl_3$), and (c) TCE + the crude product of the reaction of **1a** carried out in NMP (300 MHz, $CDCl_3$).

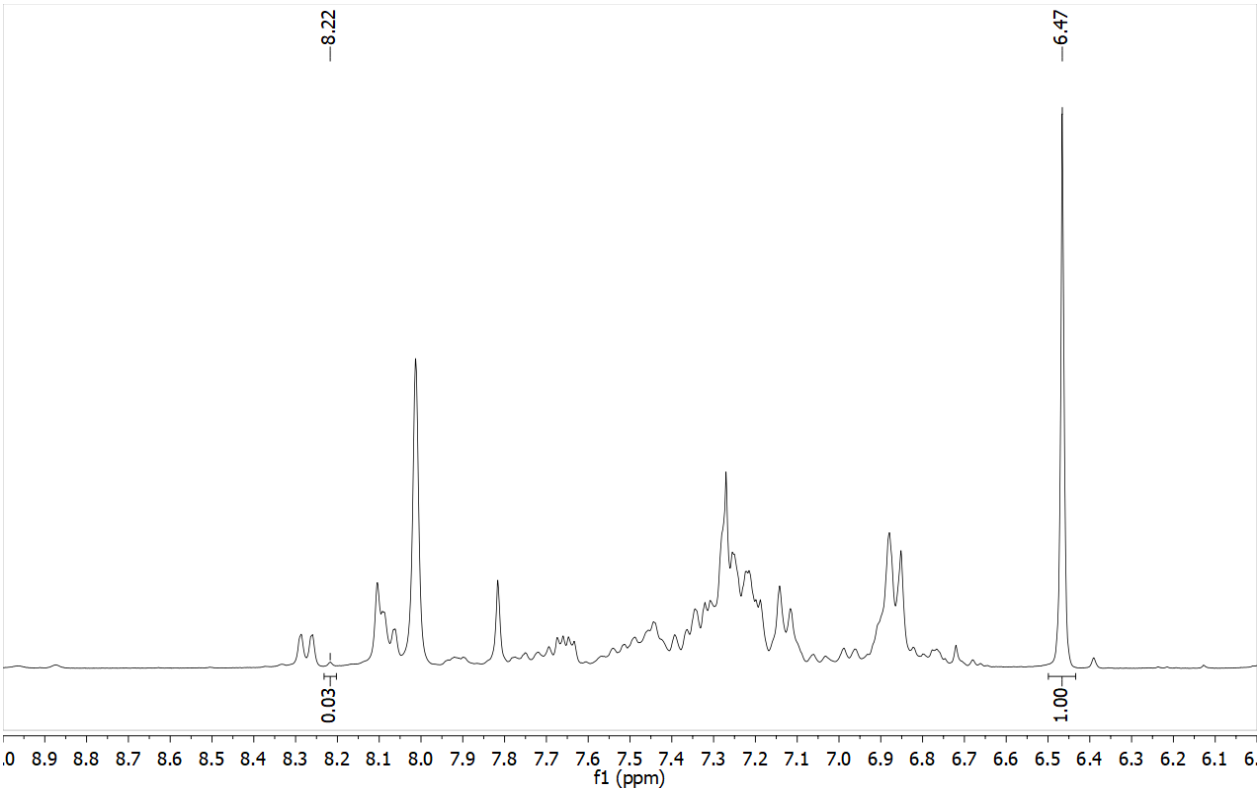


Figure S5. ^{1}H NMR spectrum of the crude product of the one pot reaction of *o*-chlorobenzaldehyde and phenylhydrazine + TCE (300 MHz, $CDCl_3$).

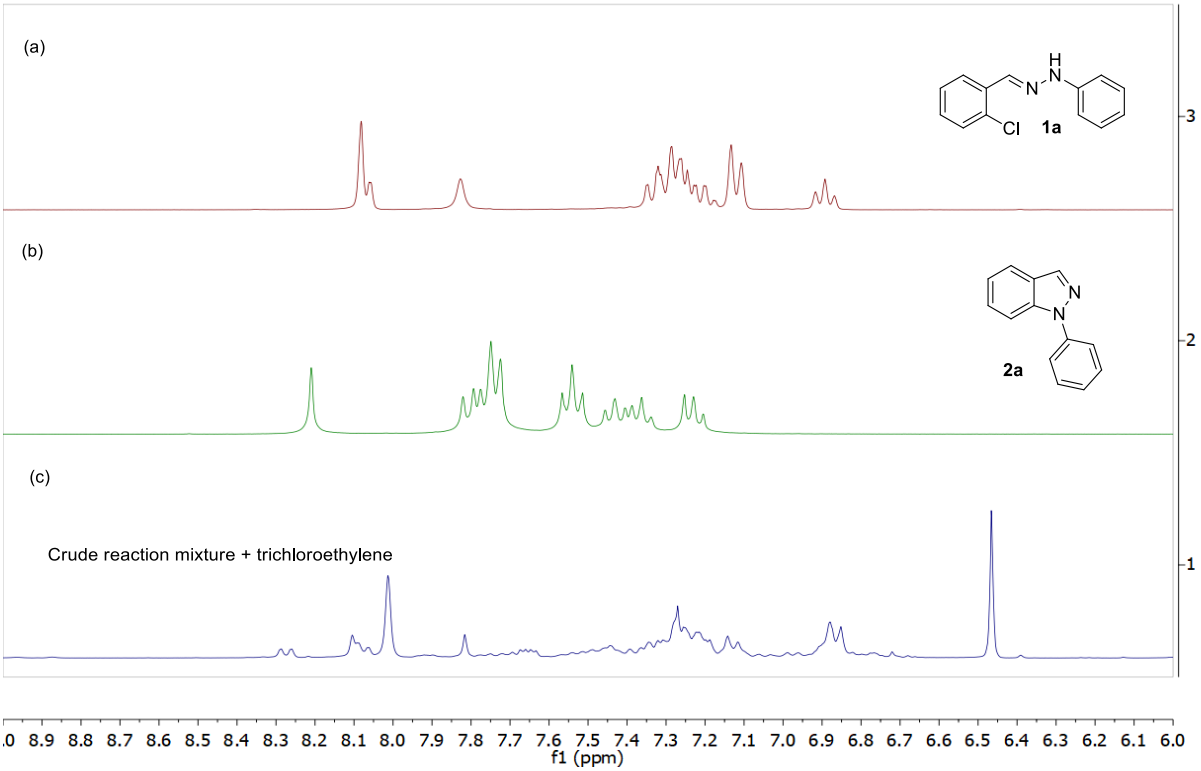


Figure S6. ^{1}H NMR spectra of (a) **1a** (300 MHz, $CDCl_3$), (b) **2a** (300 MHz, $CDCl_3$), and (c) TCE + the crude product of the one pot reaction of *o*-chlorobenzaldehyde and phenylhydrazine (300 MHz, $CDCl_3$).

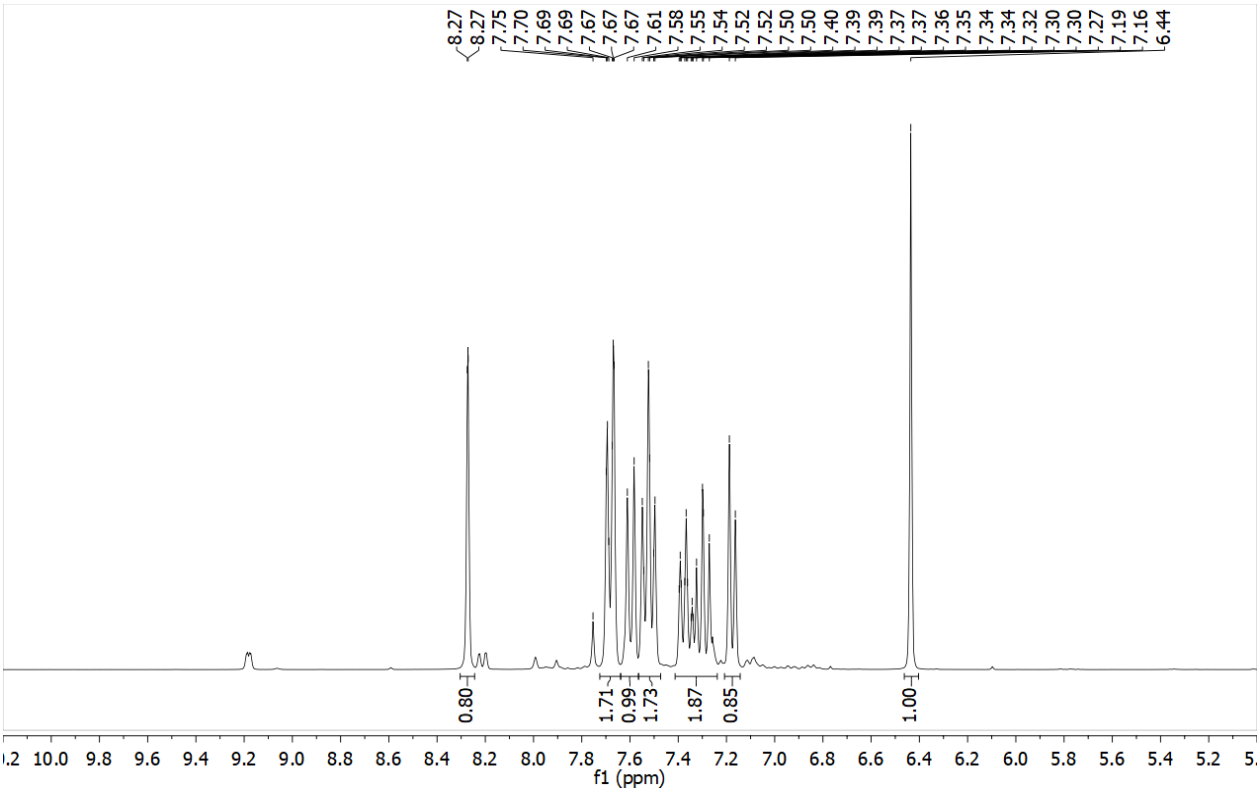


Figure S7. ^{1}H NMR spectrum of the crude product of the reaction of **1i** without CuI + TCE (300 MHz, $CDCl_3$).

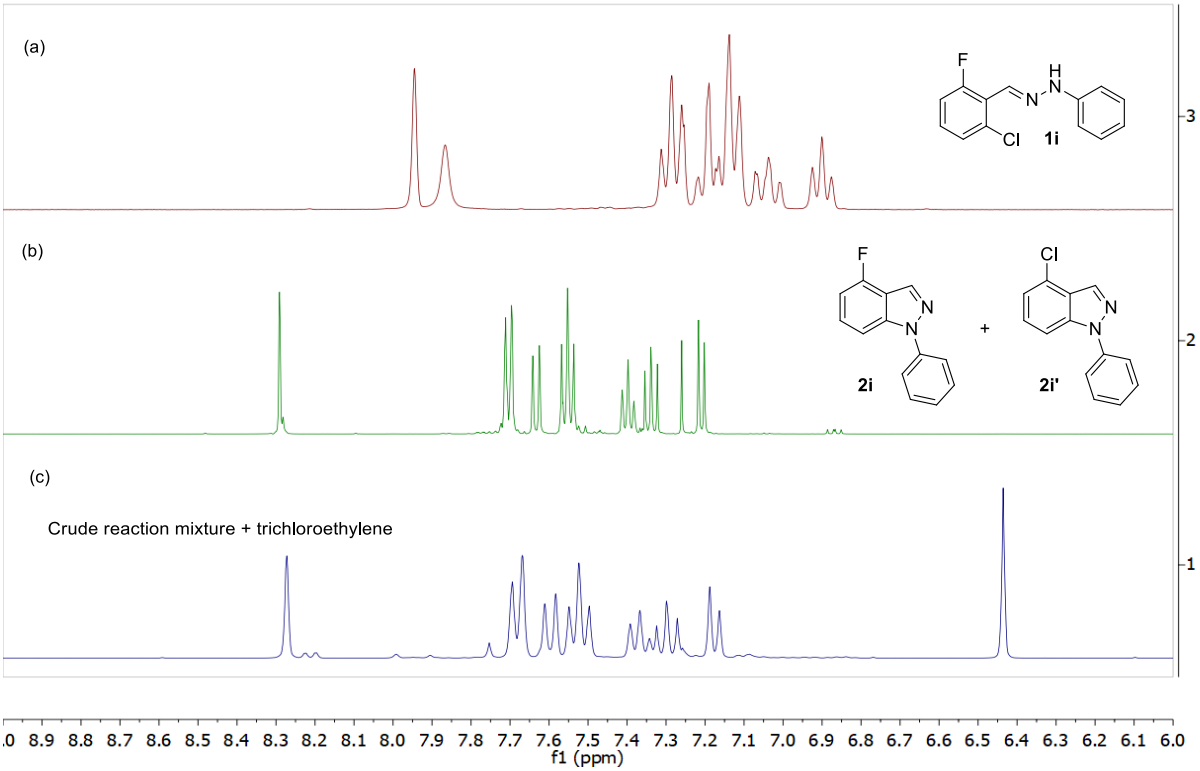


Figure S8. ^{1}H NMR spectra of (a) **1i** (300 MHz, $CDCl_3$), (b) mixture of **2i** and **2i'** (500 MHz, $CDCl_3$), and (c) TCE + the crude product of the reaction of **1i** without CuI (300 MHz, $CDCl_3$).

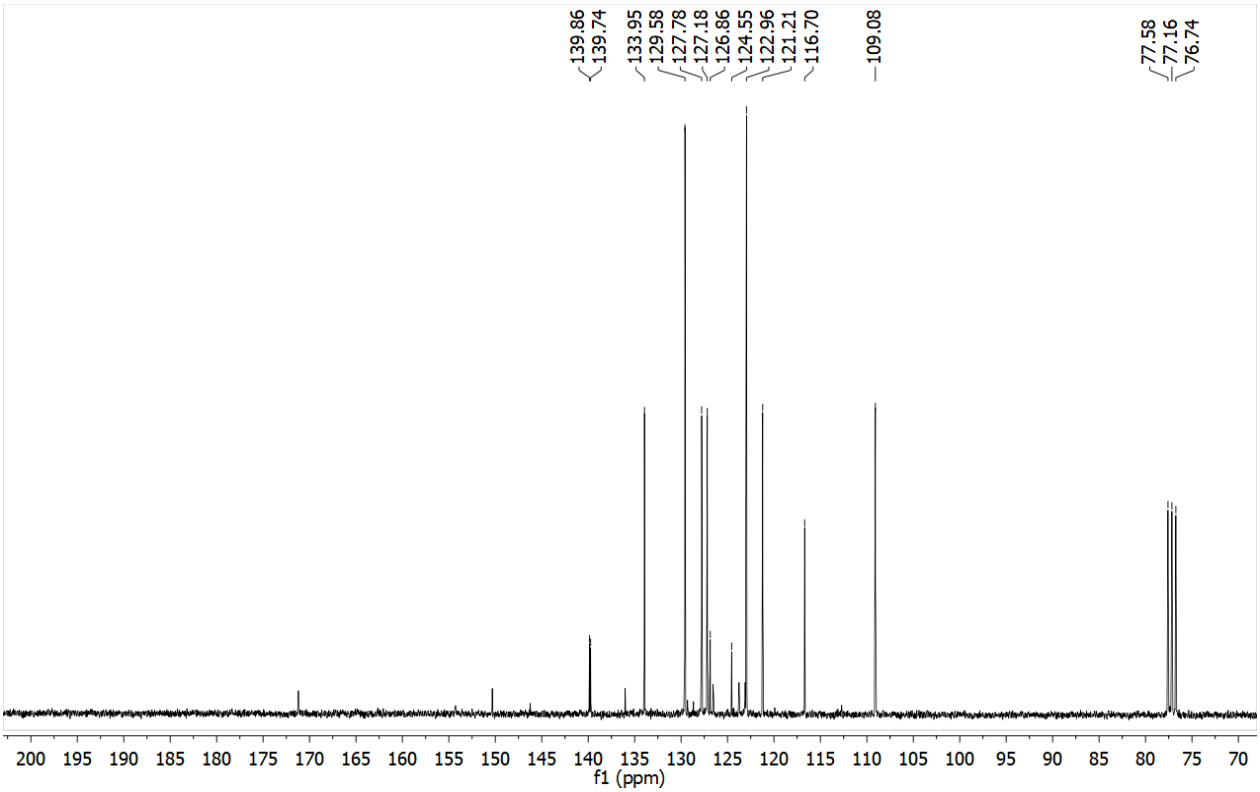


Figure S9. ^{13}C NMR spectrum of the crude product of the reaction of **1i** without CuI + TCE (75 MHz, $CDCl_3$).

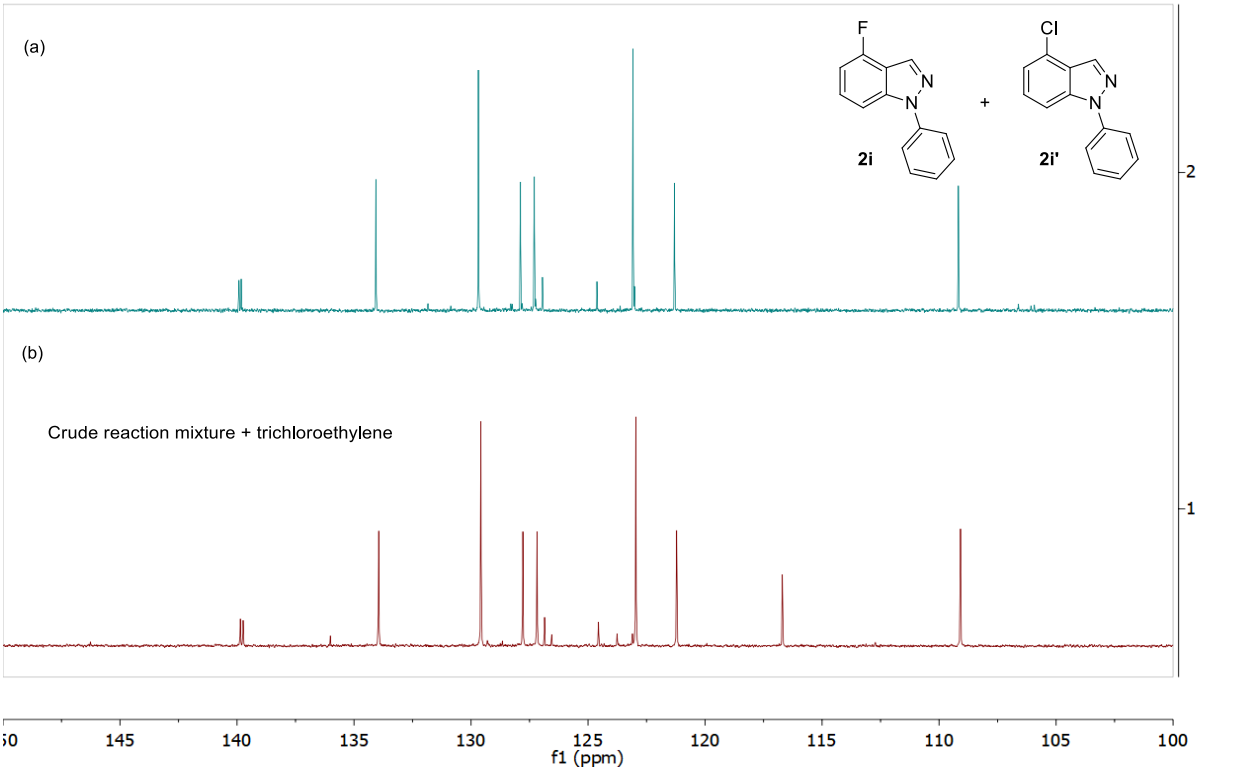


Figure S10. ^{13}C NMR spectra of (a) mixture of **2i** and **2i'** (100 MHz, $CDCl_3$) and (b) TCE + the crude product of the reaction of **1i** without CuI (75 MHz, $CDCl_3$).

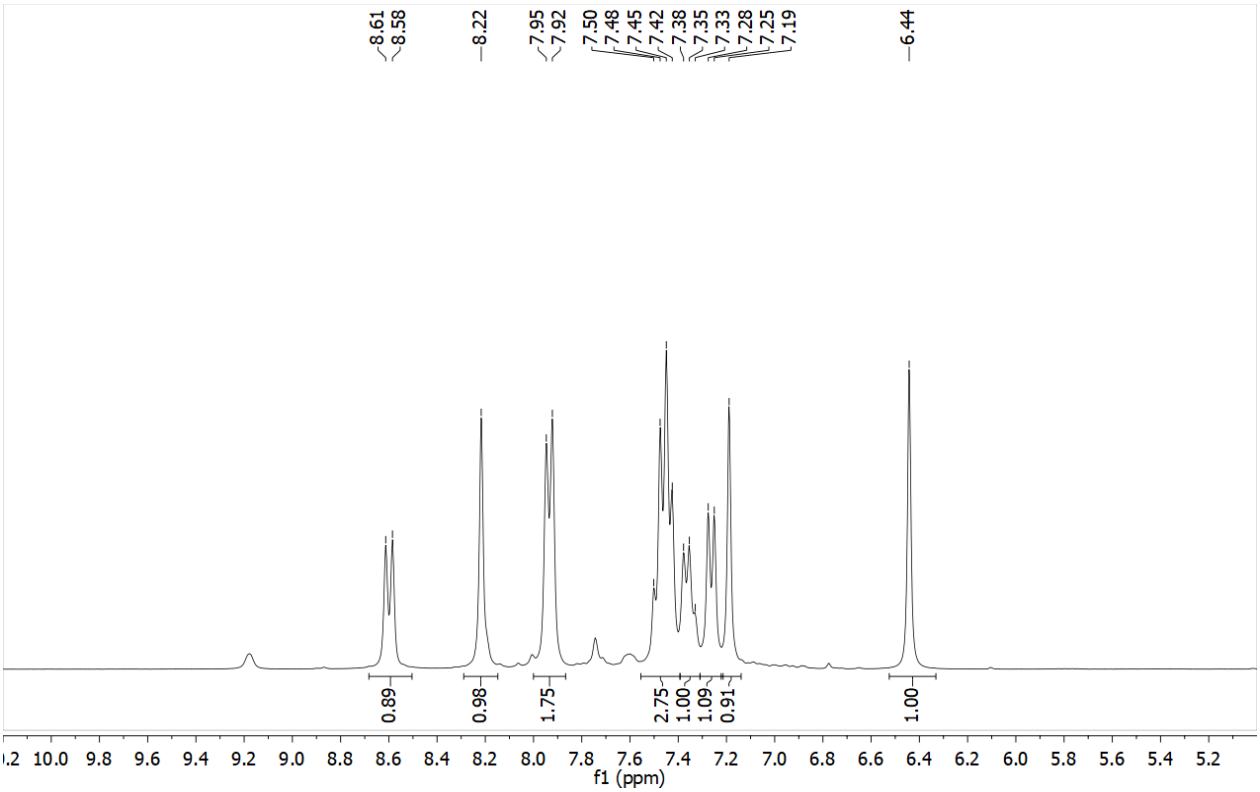


Figure S11. ^{1}H NMR spectrum of the crude product of the reaction of **3i** without CuI + TCE (300 MHz, $CDCl_3$).

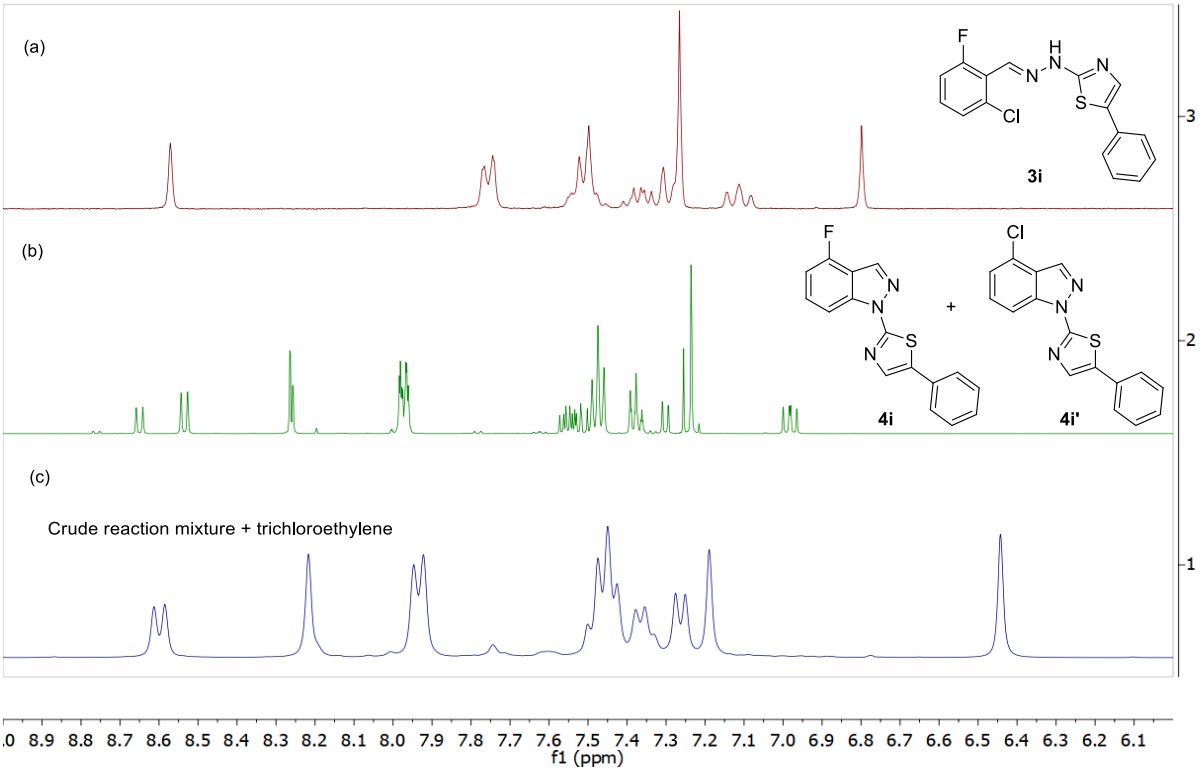


Figure S12. ^{1}H NMR spectra of (a) **3i** (300 MHz, $CDCl_3$), (b) mixture of **4i** and **4i'** (500 MHz, $CDCl_3$), and (c) TCE + the crude product of the reaction of **3i** without CuI (300 MHz, $CDCl_3$).

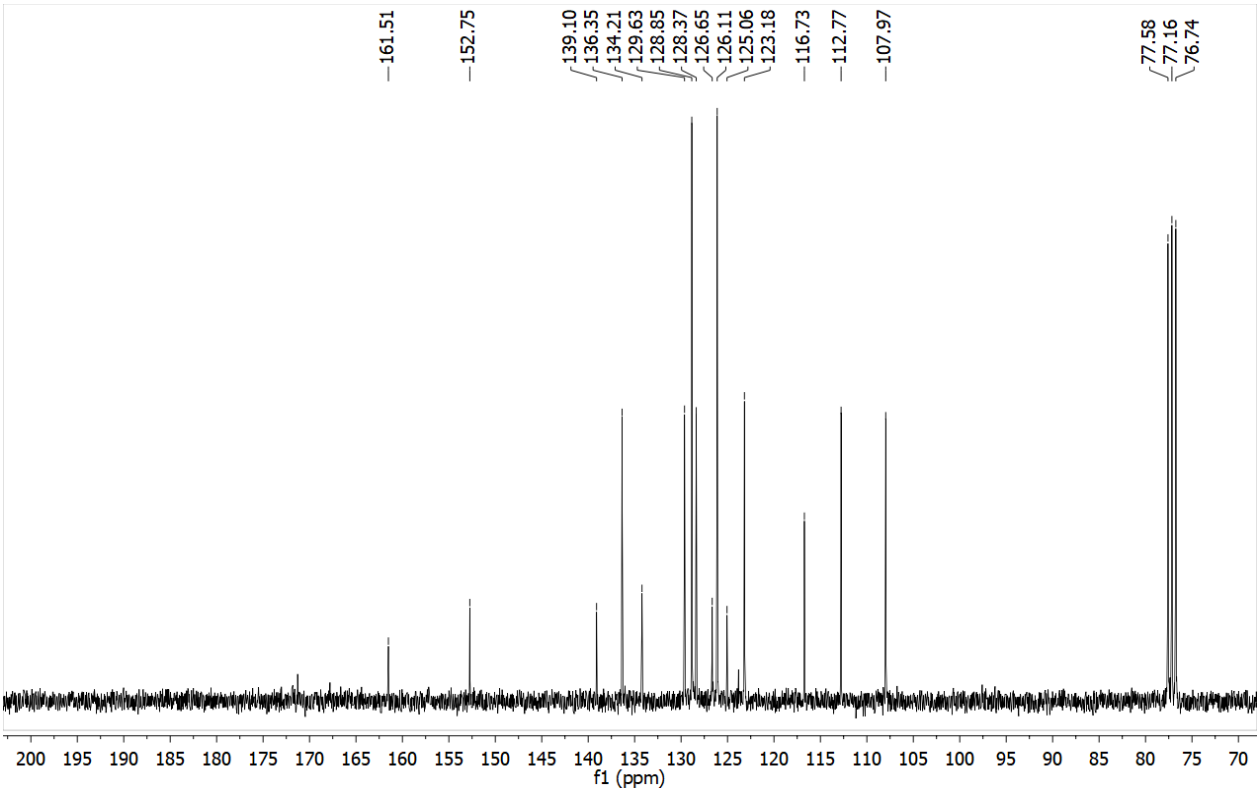


Figure S13. ^{13}C NMR spectrum of the crude product of the reaction of **3i** without CuI + TCE (75 MHz, $CDCl_3$).

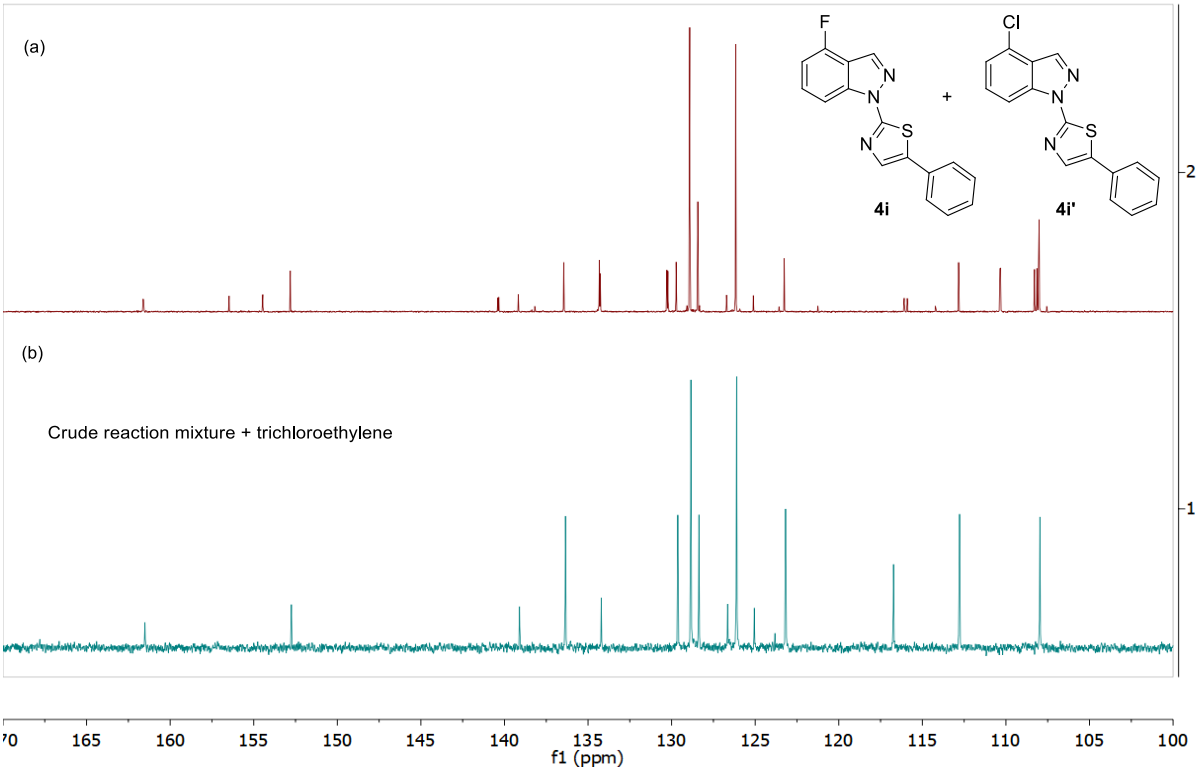


Figure S14. ^{13}C NMR spectra of (a) mixture of **4i** and **4i'** (75 MHz, $CDCl_3$) and (b) TCE + the crude product of the reaction of **3i** without CuI (100 MHz, $CDCl_3$).

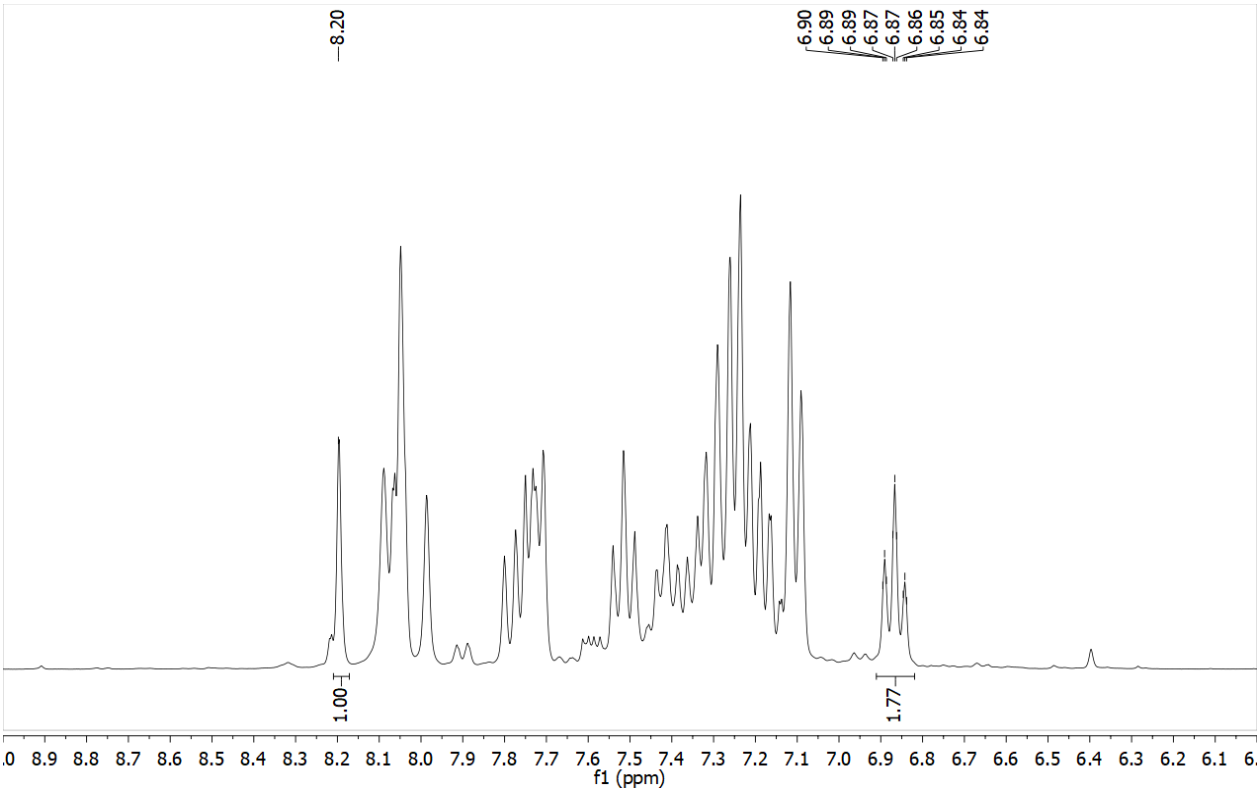


Figure S15. ^{1}H NMR spectrum of the crude product of the reaction of **1a** carried out in gram scale (300 MHz, $CDCl_3$).

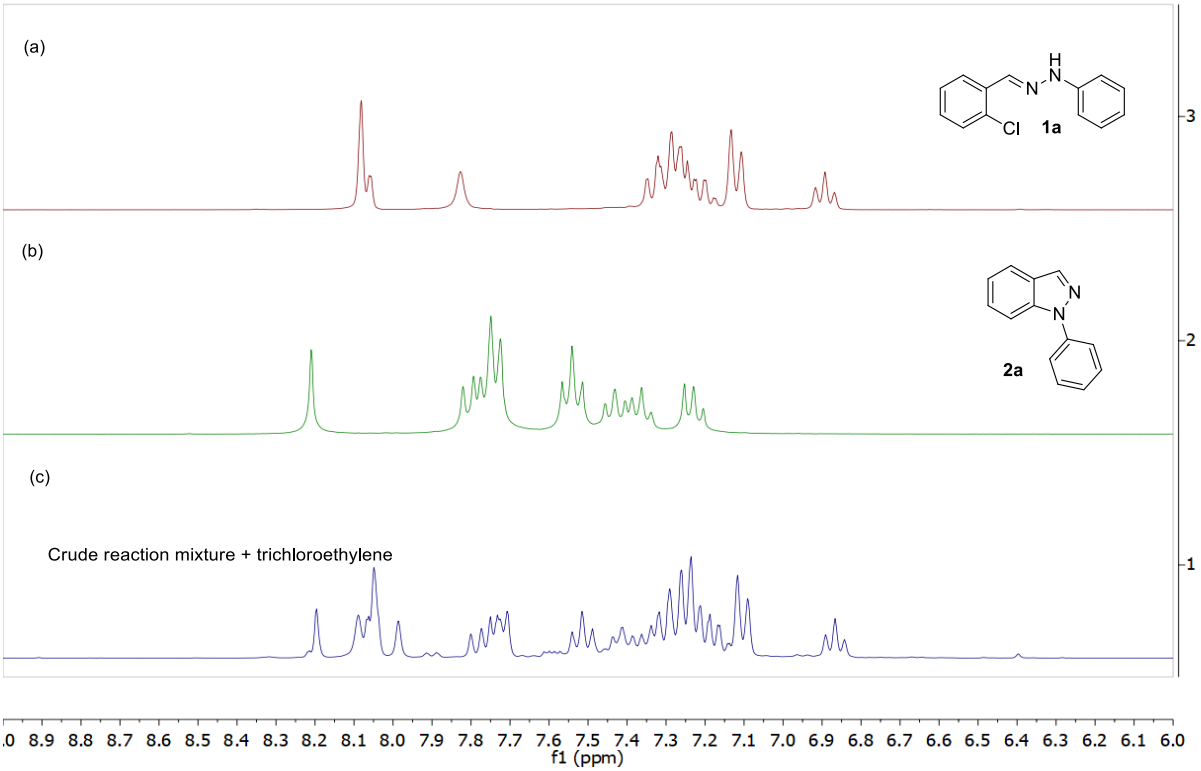
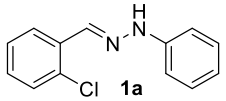


Figure S16. ^{1}H NMR spectra of (a) **1a** (300 MHz, $CDCl_3$), (b) **2a** (300 MHz, $CDCl_3$), and (c) the crude product of the reaction of **1a** carried out in gram scale (300 MHz, $CDCl_3$).

Characterization data of compounds 1–4

Characterization data of hydrazones 1a–i

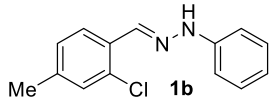
(*Z*,*E*)-1-(2-Chlorobenzylidene)-2-phenylhydrazine (**1a**) [CAS number 34158-76-4]



1a

Yellowish solid, yield 1.016 g (88%), mp 77–79 °C (lit. 84.7–85.5 °C [1]). HRMS (ESI-TOF) for $C_{13}H_{12}ClN_2$ $[M+H]^+$ calcd. 231.0684, found 231.0669.

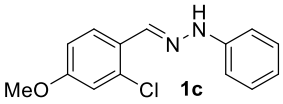
(*Z*,*E*)-1-(2-Chloro-4-methylbenzylidene)-2-phenylhydrazine (**1b**)



1b

Yellowish solid, yield 1.043 g (85%), mp 90–93 °C. HRMS (ESI-TOF) for $C_{14}H_{14}ClN_2$ $[M+H]^+$ calcd. 245.0840, found 245.0836.

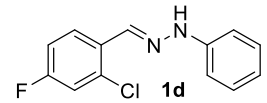
(*Z*,*E*)-1-(2-Chloro-4-methoxybenzylidene)-2-phenylhydrazine (**1c**)



1c

Yellowish solid, yield 1.203 g (92%), mp 100–102 °C. HRMS (ESI-TOF) for $C_{14}H_{14}ClN_2O$ $[M+H]^+$ calcd. 261.0789, found 261.0798.

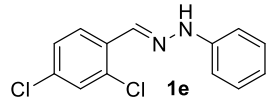
(*Z*,*E*)-1-(2-Chloro-4-fluorobenzylidene)-2-phenylhydrazine (**1d**)



1d

Yellowish solid, yield 1.130 g (90%), mp 99–101 °C. HRMS (ESI-TOF) for $C_{13}H_{11}ClFN_2$ $[M+H]^+$ calcd. 249.0589, found 249.0588.

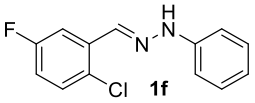
(*Z*,*E*)-1-(2,4-Dichlorobenzylidene)-2-phenylhydrazine (**1e**) [CAS number 21719-63-1]



1e

Yellowish solid, yield 1.277 g (96%), mp 150–153 °C. HRMS (ESI-TOF) for $C_{13}H_{11}Cl_2N_2$ $[M+H]^+$ calcd. 265.0294, found 265.0284.

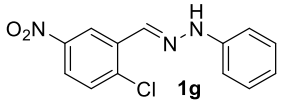
(*Z*,*E*)-1-(2-Chloro-5-fluorobenzylidene)-2-phenylhydrazine (**1f**)



1f

Yellowish solid, yield 1.214 g (97%), mp 80–85 °C. HRMS (ESI-TOF) for $C_{13}H_{11}ClFN_2$ $[M+H]^+$ calcd. 249.0589, found 249.0594.

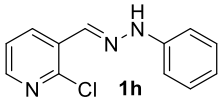
(*Z*,*E*)-1-(2-Chloro-5-nitrobenzylidene)-2-phenylhydrazine (**1g**) [CAS number 59670-70-1]



1g

Yellowish solid, yield 0.914 g (66%), mp 173−176 °C (lit. 105−108 °C [2]). HRMS (ESI-TOF) for $C_{13}H_{11}ClN_3O_2$ $[M+H]^+$ calcd. 276.0534, found 276.0530.

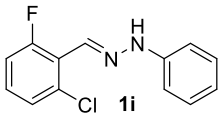
(*Z*,*E*)-2-Chloro-3-((2-phenylhydrazono)methyl)pyridine (**1h**)



1h

Yellowish solid, yield 1.025 g (88%), mp 200−203 °C. HRMS (ESI-TOF) for $C_{12}H_{11}ClN_3$ $[M+H]^+$ calcd. 232.0636, found 232.0644.

(*Z*,*E*)- 1-(2-Chloro-6-fluorobenzylidene)-2-phenylhydrazine (**1i**) [CAS number 674348-42-6]

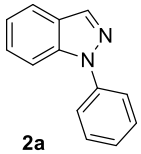


1i

Yellowish solid, yield 1.121 g (90%), mp 78−82 °C. HRMS (ESI-TOF) for $C_{13}H_{11}ClFN_2$ $[M+H]^+$ calcd. 249.0589, found 249.0594.

Characterization data of indazoles 2a,b,d–i,i'

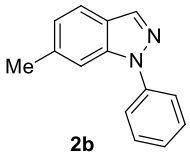
1-Phenyl-1*H*-indazole (**2a**) [CAS number 7788-69-4]



2a

Yellowish solid, yield 0.058 g (60%), mp 92−94 °C (lit. 78−80 °C [3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.82–7.72 (m, 4H), 7.57–7.51 (m, 2H), 7.46–7.34 (m, 2H), 7.25–7.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 138.9, 135.5, 129.6, 127.3, 126.8, 125.4, 122.9, 121.6, 121.5, 110.6; HRMS (ESI-TOF) for $C_{13}H_{11}N_2$ $[M+H]^+$ calcd. 195.0917, found 195.0922.

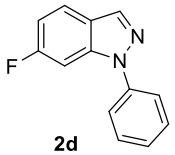
6-Methyl-1-phenyl-1*H*-indazole (**2b**) [CAS number 838820-88-5]



2b

Brownish solid; yield 0.010 g (10%), mp 91−93 °C (lit. 86−87 °C [3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.74–7.66 (m, 3H), 7.57–7.66 (m, 3H), 7.39–7.33 (m, 1H), 7.08–7.05 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 139.5, 137.7, 135.4, 129.6, 126.7, 123.8, 123.6, 122.9, 121.0, 110.0, 22.3. HRMS (ESI-TOF) for $C_{14}H_{13}N_2$ $[M+H]^+$ calcd. 209.1073, found 209.1059.

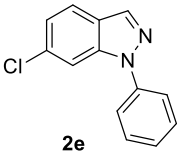
4.3.3. 6-Fluoro-1-phenyl-1*H*-indazole (**2d**) [CAS number 1521657-52-2]



2d

Brownish solid; yield 0.025 g (23%), mp 75−77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 1.0 Hz, 1H), 7.74 (dd, J = 8.8, 5.2 Hz, 1H), 7.70–7.67 (m, 2H), 7.58–7.52 (m, 2H), 7.41–7.35 (m, 2H), 7.01 (td, J = 8.9, 2.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (d, J = 245.5 Hz), 139.9, 139.2 (d, J = 12.5 Hz), 135.6, 129.7, 127.1, 122.8 (d, J = 11.0 Hz), 122.8, 122.2, 111.5 (d, J = 26.0 Hz), 96.6 (d, J = 27.4 Hz). HRMS (ESI-TOF) for $C_{13}H_{10}FN_2$ $[M+H]^+$ calcd. 213.0823, found 213.0809.

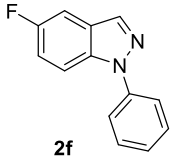
6-Chloro-1-phenyl-1*H*-indazole (**2e**) [CAS number 1582296-38-5]



2e

Yellowish solid, yield 0.045 g (39%), mp 89−91 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.40 (d, J = 1.1 Hz, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.84–7.83 (m, 1H), 7.77–7.74 (m, 2H), 7.61–7.56 (m, 2H), 7.44–7.38 (m, 1H), 7.27 (dd, J = 8.6, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 139.2, 138.4, 135.9, 132.6, 129.7, 127.0, 123.8, 123.1, 122.3, 110.0; HRMS (ESI-TOF) for $C_{13}H_{10}ClN_2$ $[M+H]^+$ calcd. 229.0527, found 229.0526.

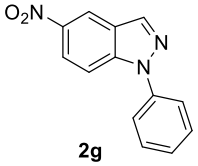
5-Fluoro-1-phenyl-1*H*-indazole (**2f**) [CAS number 350044-22-3]



2f

Brownish solid, yield 0.056 g (53%), mp 56−58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 1.0 Hz, 1H), 7.72–7.68 (m, 3H), 7.57–7.53 (m, 2H), 7.43–7.37 (m, 2H), 7.21 (td, J = 9.0, 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3 (d, J = 239.4 Hz), 140.0, 135.9, 135.1 (d, J = 5.5 Hz), 129.7, 127.1, 125.5 (d, J = 10.3 Hz), 122.8, 116.7 (d, J = 27.4 Hz), 111.7 (d, J = 9.5 Hz), 105.4 (d, J = 23.5 Hz). HRMS (ESI-TOF) for $C_{13}H_{10}FN_2$ $[M+H]^+$ calcd. 213.0823, found 213.0830.

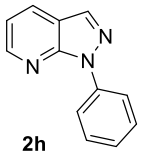
5-Nitro-1-phenyl-1*H*-indazole (**2g**) [CAS number 838821-02-6]



2g

Yellowish solid, yield 0.019 g (16%), mp 184−186 °C (lit. 178−180 °C [2]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (dd, J = 2.1, 0.7 Hz, 1H), 8.42 (d, J = 0.9 Hz, 1H), 8.32 (dd, J = 9.3, 2.1 Hz, 1H), 7.79 (dt, J = 9.2, 0.8 Hz, 1H), 7.73–7.70 (m, 2H), 7.62–7.59 (m, 2H), 7.49–7.45 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 140.7, 139.1, 137.7, 129.9, 128.1, 124.6, 123.3, 122.4, 119.2, 110.9; HRMS (ESI-TOF) for $C_{13}H_{10}N_3O_2$ $[M+H]^+$ calcd. 240.0768, found 240.0760.

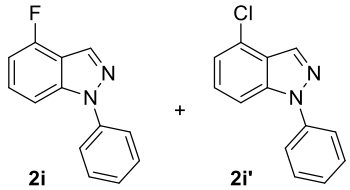
1-Phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (**2h**) [CAS number 20208-81-5]



2h

Redwish solid, yield 0.068 g (70%), mp 68−70 °C (lit. 53−55 °C [3]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (dd, J = 4.5, 1.6 Hz, 1H), 8.27–8.25 (m, 2H), 8.21 (s, 1H), 8.13 (dd, J = 8.0, 1.7 Hz, 1H), 7.56–7.52 (m, 2H), 7.35–7.31 (m, 1H), 7.22 (dd, J = 8.0, 4.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 149.3, 139.5, 134.0, 130.4, 129.3, 126.3, 121.5, 117.8, 117.3; HRMS (ESI-TOF) for $C_{12}H_{10}N_3$ $[M+H]^+$ calcd. 196.0866, found 196.0869.

4-Fluoro-1-phenyl-1*H*-indazole (**2i**) + 4-chloro-1-phenyl-1*H*-indazole (**2i'**) [CAS number 861327-91-5]

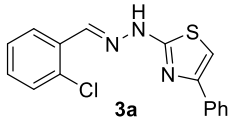


2i + **2i'**

HRMS (ESI-TOF) for $C_{13}H_{10}FN_2$ $[M+H]^+$ calcd. 213.0823, found 213.0817. HRMS (ESI-TOF) for $C_{13}H_{10}ClN_2$ $[M+H]^+$ calcd. 229.0527, found 229.0525.

Characterization data of hydrazones 3a–i

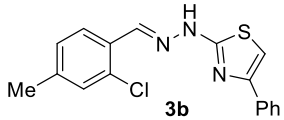
(*Z*,*E*)-2-(2-(2-Chlorobenzylidene)hydrazinyl)-4-phenylthiazole (**3a**) [CAS number 324066-80-0]



3a

Pale yellow solid, yield 0.445 mg (94%), mp 205−208 °C (lit. 220−221 °C [4]). HRMS (ESI-TOF) for $C_{16}H_{13}ClN_3S$ $[M+H]^+$ calcd. 314.0513, found 314.0504.

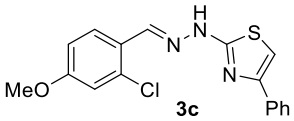
(*Z*,*E*)-2-(2-(2-Chloro-4-methylbenzylidene)hydrazinyl)-4-phenylthiazole (**3b**)



3b

Whitish solid, yield 0.356 g (72%), mp 220−223 °C; HRMS (ESI-TOF) for $C_{17}H_{15}ClN_3S$ $[M+H]^+$ calcd. 328.0670, found 328.0689.

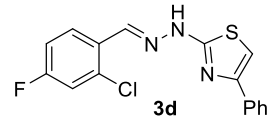
(*Z*,*E*)-2-(2-(2-Chloro-4-methoxybenzylidene)hydrazinyl)-4-phenylthiazole (**3c**)



3c

Pale yellow solid, yield 0.415 g (80%), mp 190−193 °C. HRMS (ESI-TOF) for $C_{17}H_{15}ClN_3OS$ $[M+H]^+$ calcd. 344.0619, found 344.0614.

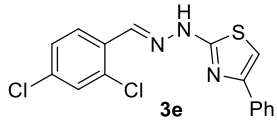
(*Z*,*E*)-2-(2-(2-Chloro-4-fluorobenzylidene)hydrazinyl)-4-phenylthiazole (**3d**)



3d

Yellowish solid, yield 0.483 g (97%), mp 210−213 °C. HRMS (ESI-TOF) for $C_{16}H_{12}ClFN_3S$ $[M+H]^+$ calcd. 332.0419, found 332.0431.

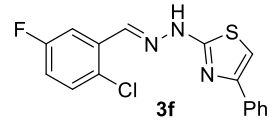
(*Z*,*E*)-2-(2-(2,4-Dichlorobenzylidene)hydrazinyl)-4-phenylthiazole (**3e**) [CAS number 339284-43-4]



3e

Pale yellow solid, yield 0.396 g (75%), mp 207−210 °C (lit. 244−246 °C [5]). HRMS (ESI-TOF) for $C_{16}H_{12}Cl_2N_3S$ $[M+H]^+$ calcd. 348.0124, found 348.0126.

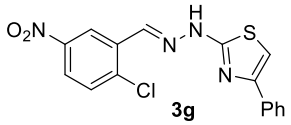
(*Z*,*E*)-2-(2-(2-Chloro-5-fluorobenzylidene)hydrazinyl)-4-phenylthiazole (**3f**)



3f

Whitish solid, yield 0.451 g (90%), mp 185−188 °C. HRMS (ESI-TOF) for $C_{16}H_{12}ClFN_3S$ $[M+H]^+$ calcd. 332.0419, found 332.0411.

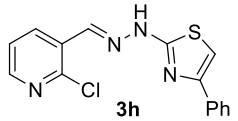
(*Z*,*E*)-2-(2-(2-Chloro-5-nitrobenzylidene)hydrazinyl)-4-phenylthiazole (**3g**) [CAS number 1684423-73-1]



3g

Yellowish solid, yield 0.375 g (70%), mp 190−192 °C. HRMS (ESI-TOF) for $C_{16}H_{12}ClN_4O_2S$ $[M+H]^+$ calcd. 359.0364, found 359.0355.

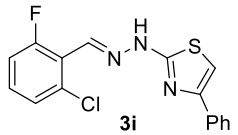
(*Z*,*E*)-2-(2-((2-Chloropyridin-3-yl)methylene)hydrazinyl)-4-phenylthiazole (**3h**)



3h

Yellowish solid, yield 0.427 g (91%), mp 225−230 °C. HRMS (ESI-TOF) for $C_{15}H_{12}ClN_4S$ $[M+H]^+$ calcd. 315.0466, found 315.0472.

(*Z*,*E*)-2-(2-(2-Chloro-6-fluorobenzylidene)hydrazinyl)-4-phenylthiazole (**3i**) [CAS number 405924-76-7]

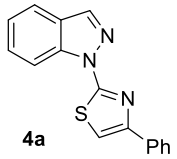


3i

Whitish solid, yield 0.484 g (97%), mp 200−203 °C. HRMS (ESI-TOF) for $C_{16}H_{12}ClFN_3S$ $[M+H]^+$ calcd. 332.0419, found 332.0419.

Characterization data of indazoles 2a,d–i,i'

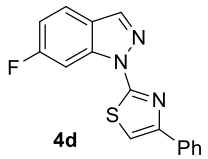
2-(1*H*-Indazol-1-yl)-4-phenylthiazole (**4a**)



4a

Brownish solid, yield 0.049 g (35%), mp 160–163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79–8.77 (m, 1H), 8.22 (d, J = 0.9 Hz, 1H), 8.02–8.00 (m, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.66–7.63 (m, 1H), 7.51–7.48 (m, 2H), 7.40–7,34 (m, 2H), 7.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 152.8, 138.4, 138.2, 134.5, 129.1, 128.9, 128.4, 126.2, 126.0, 123.6, 121.3, 114.2, 107.6; HRMS (ESI-TOF) for $C_{16}H_{12}N_3S$ $[M+H]^+$ calcd. 278.0746, found 278.0746.

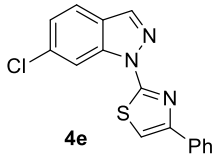
2-(6-Fluoro-1*H*-indazol-1-yl)-4-phenylthiazole (**4d**)



4d

Brownish solid, yield 0.018 g (12%), mp 129–132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (ddd, J = 9.4, 1.8, 1.0 Hz, 1H), 8.16 (d, J = 0.9 Hz, 1H), 7.99–7.97 (m, 2H), 7.73 (dd, J = 8.8, 5.0 Hz, 1H), 7.50– 7.47 (m, 2H), 7.40–7.37 (m, 1H), 7.23 (s, 1H), 7.11 (td, J = 8.9, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (d, J = 247.5 Hz), 161.6, 152.8, 138.7 (d, J = 13.9 Hz), 138.0, 134.2, 129.0, 128.4, 126.2, 122,6, 122,6 (d, J = 11.0 Hz), 113.2 (d, J = 26.0 Hz), 107.8, 100.6 (d, J = 28.2 Hz); HRMS (ESI-TOF) for $C_{16}H_{11}FN_3S$ $[M+H]^+$ calcd. 296.0652, found 296.0640.

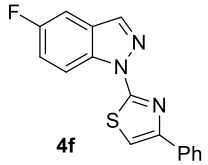
2-(6-Chloro-1*H*-indazol-1-yl)-4-phenylthiazole (**4e**)



4e

Yellowish solid, yield 0.037 g (23%), mp 140–143 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (dd, J = 1.7, 0.9 Hz, 1H), 8.14 (d, J = 0.8 Hz, 1H), 7.97–7.95 (m, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.50–7.47 (m, 2H), 7.40–7.36 (m, 1H), 7.29 (dd, J = 8.5, 1.8 Hz, 1H), 7.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 152.8, 138.5, 137.9, 135.4, 134.2, 129.0, 128.4, 126.2, 124.6, 124.4, 122.0, 114.1, 107.9; HRMS (ESI-TOF) for $C_{16}H_{11}ClN_3S$ $[M+H]^+$ calcd. 312.0357, found 312.0362.

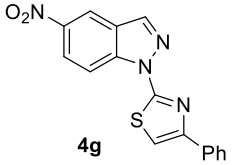
2-(5-Fluoro-1*H*-indazol-1-yl)-4-phenylthiazole (**4f**)



4f

Yellowish solid, yield 0.036 g (24%), mp 165–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (ddt, J = 9.0, 4.4, 0.8 Hz, 1H), 8.16 (d, J = 1.0 Hz, 1H), 7.99–7.97 (m, 2H), 7.52–7.46 (m, 2H), 7.42–7.36 (m, 3H), 7.23 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.2 (d, J = 241.7 Hz), 152.7, 137,7 (d, J = 5.2 Hz), 135.3, 134.3, 128.9, 128.4, 126.2, 126.1, 118.2 (d, J = 26.5 Hz), 115.5 (d, J = 9.1 Hz), 107.8, 105.8 (d, J = 24.0 Hz); HRMS (ESI-TOF) for $C_{16}H_{11}FN_3S$ $[M+H]^+$ calcd. 296.0652, found 296.0635.

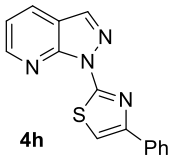
2-(5-Nitro-1*H*-indazol-1-yl)-4-phenylthiazole (**4g**)



4g

Brownish solid, yield 0.031 g (19%), mp 278–280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, J = 9.2 Hz, 1H), 8.77 (d, J = 2.1 Hz, 1H), 8.51 (dd, J = 9.3, 2.1 Hz, 1H), 8.39 (s, 1H), 8.00–7.97 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.38 (m, 1H), 7.32 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 153.2, 144.2, 140.0, 139.4, 134.0, 129.0, 128.7, 126.2, 125.3, 124.0, 118.5, 114.8, 108.8; HRMS (ESI-TOF) for $C_{16}H_{11}N_4O_2S$ $[M+H]^+$ calcd. 323.0621, found 323.0597.

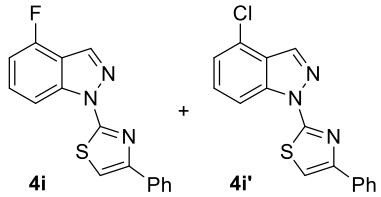
4-Phenyl-2-(1*H*-pyrazolo[3,4-*b*]pyridin-1-yl)thiazole (**4h**)



4h

Yellowish solid, yield 0.048 g (34%), mp 65–68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (dd, J = 4.6, 1.6 Hz, 1H), 8.33 (s, 1H), 8.19 (dd, J = 8.0, 1.6 Hz, 1H), 8.05–8.02 (m, 2H), 7.46–7.43 (m, 2H), 7.40 (s, 1H), 7.37–7.34 (m, 1H), 7.34 (dd, J = 7.9, 4.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 152.5, 150.2, 149.7, 136.8, 134.2, 130.9, 128.7, 128.3, 126.6, 119.1, 117.5, 109.4; HRMS (ESI-TOF) for $C_{15}H_{11}N_4S$ $[M+H]^+$ calcd. 279.0699, found 279.0700.

2-(4-Fluoro-1*H*-indazol-1-yl)-4-phenylthiazole (**4i**) + 2-(4-chloro-1*H*-indazol-1-yl)-4-phenylthiazole (**4i'**)



4i **4i'**

HRMS (ESI-TOF) for $C_{16}H_{11}FN_3S$ $[M+H]^+$ calcd. 296.0652, found 296.0651. HRMS (ESI-TOF) for $C_{16}H_{11}ClN_3S$ $[M+H]^+$ calcd. 312.0357, found 312.0353.

^{1}H and ^{13}C NMR spectra of *N*-phenyl-1*H*-indazoles

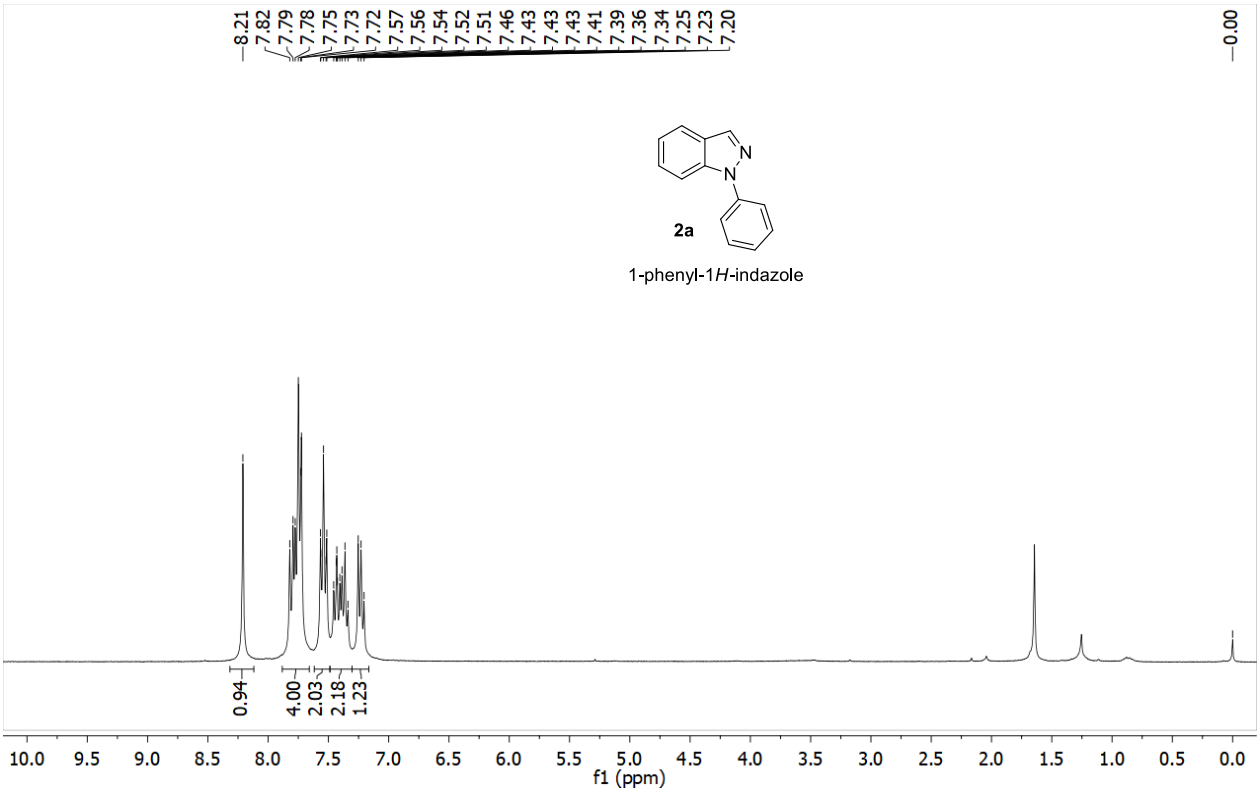


Figure S17. ^{1}H NMR spectrum of compound **2a** (300 MHz, $CDCl_3$).

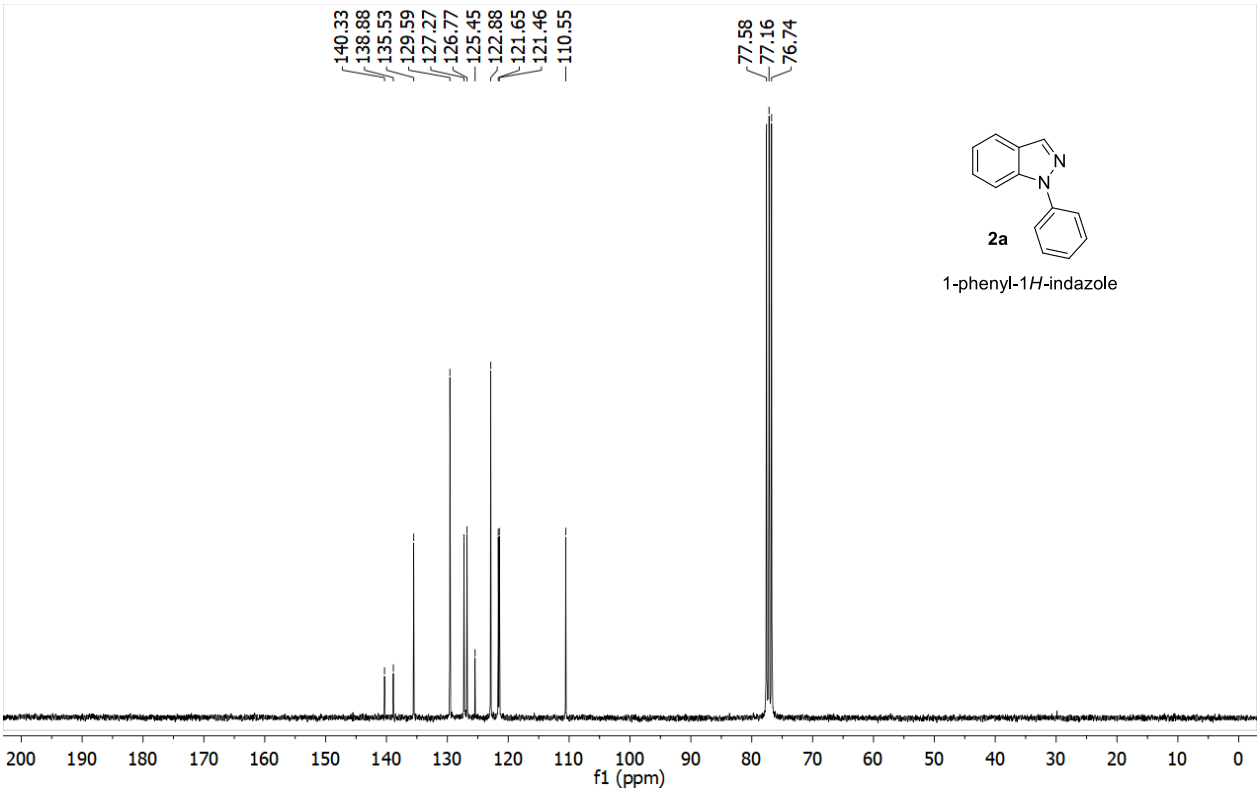


Figure S18. ^{13}C NMR spectrum of compound **2a** (75 MHz, $CDCl_3$).

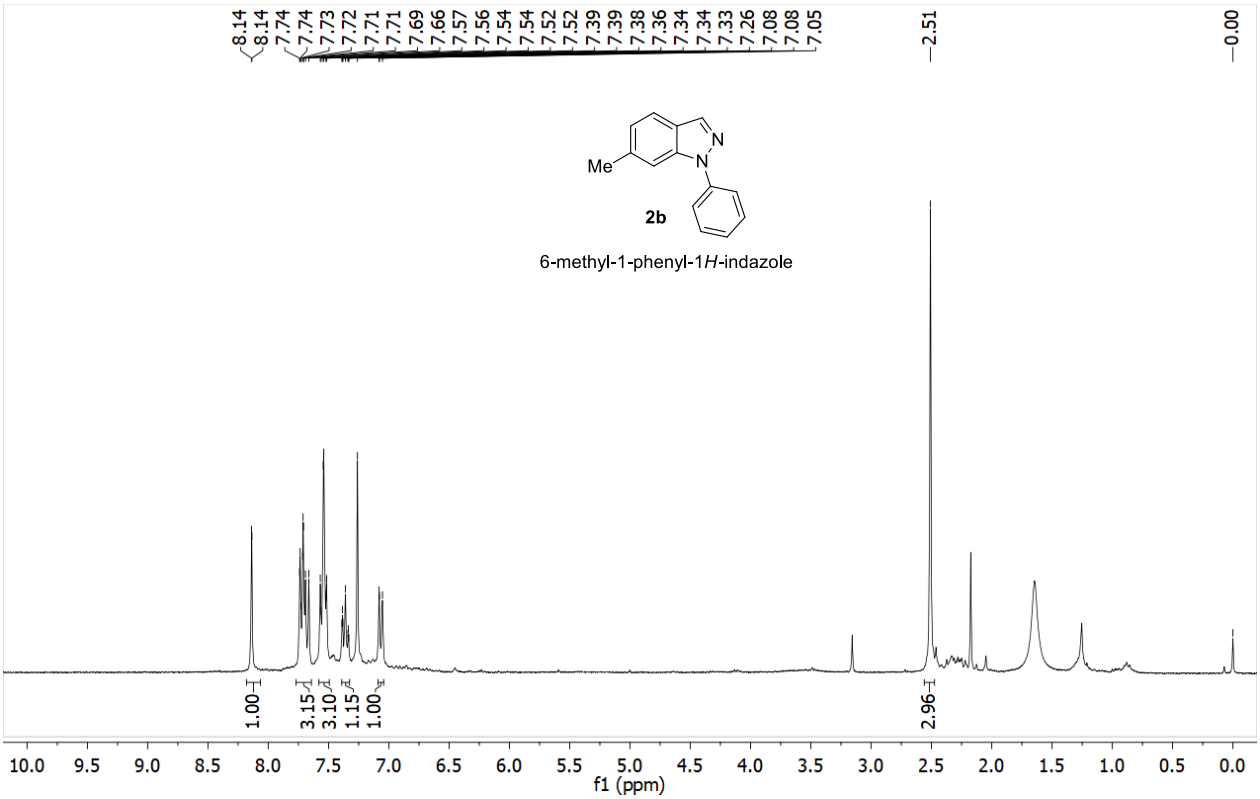


Figure S19. ^{1}H NMR spectrum of compound **2b** (300 MHz, $CDCl_3$).

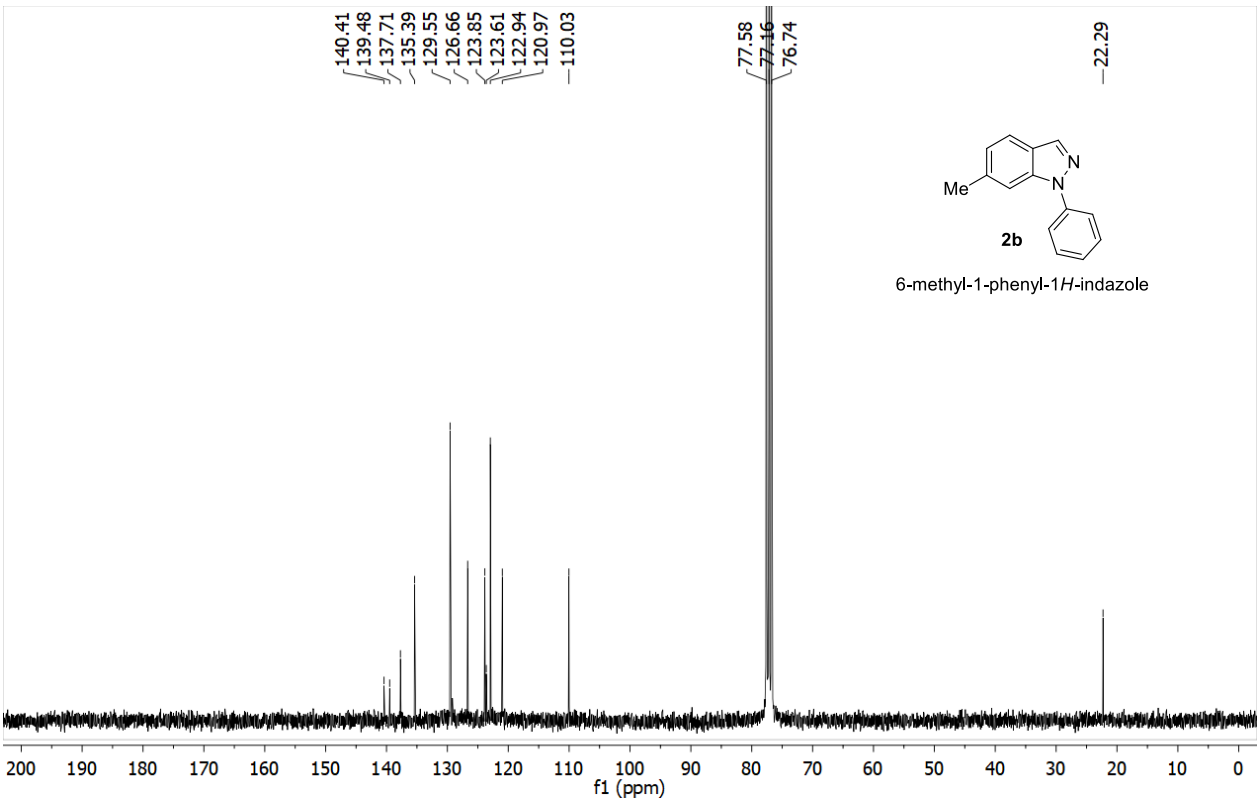


Figure S20. ^{13}C NMR spectrum of compound **2b** (75 MHz, $CDCl_3$).

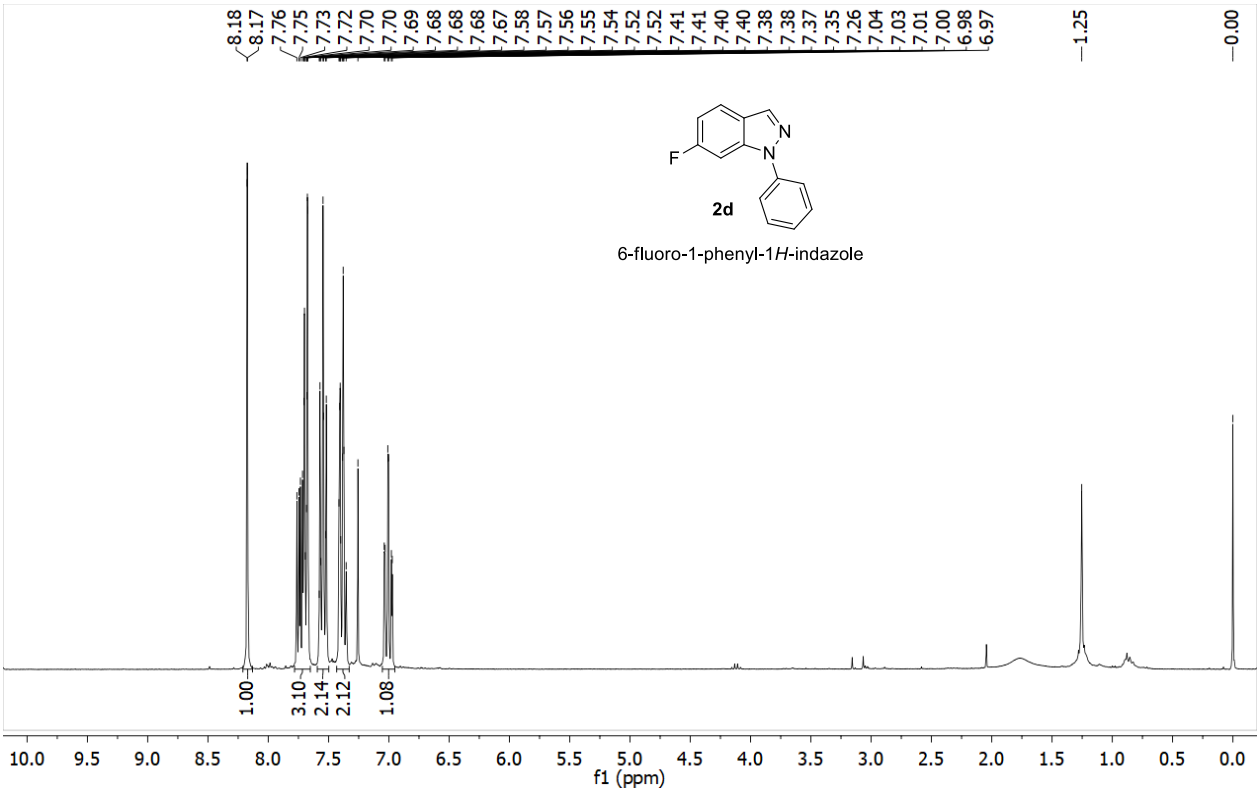


Figure S21. ^{1}H NMR spectrum of compound **2d** (300 MHz, $CDCl_3$).

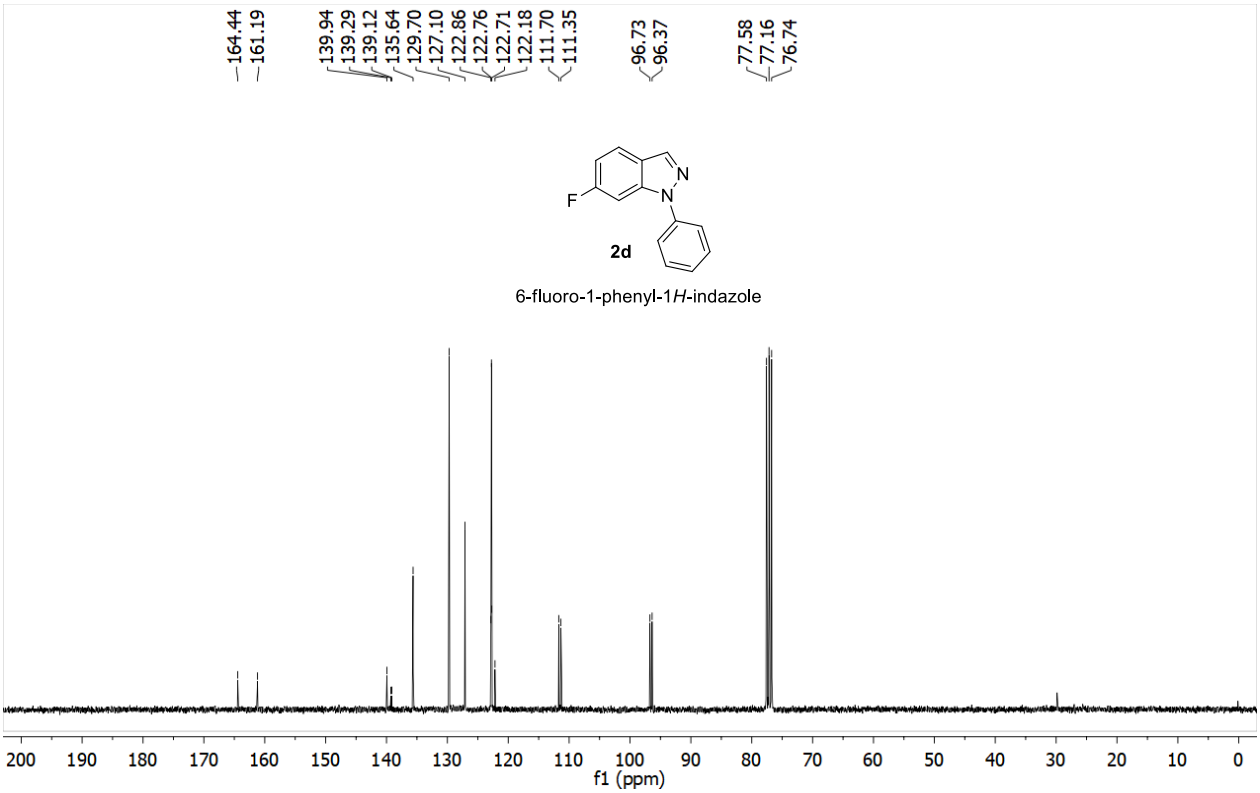


Figure S22. ^{13}C NMR spectrum of compound **2d** (75 MHz, $CDCl_3$).

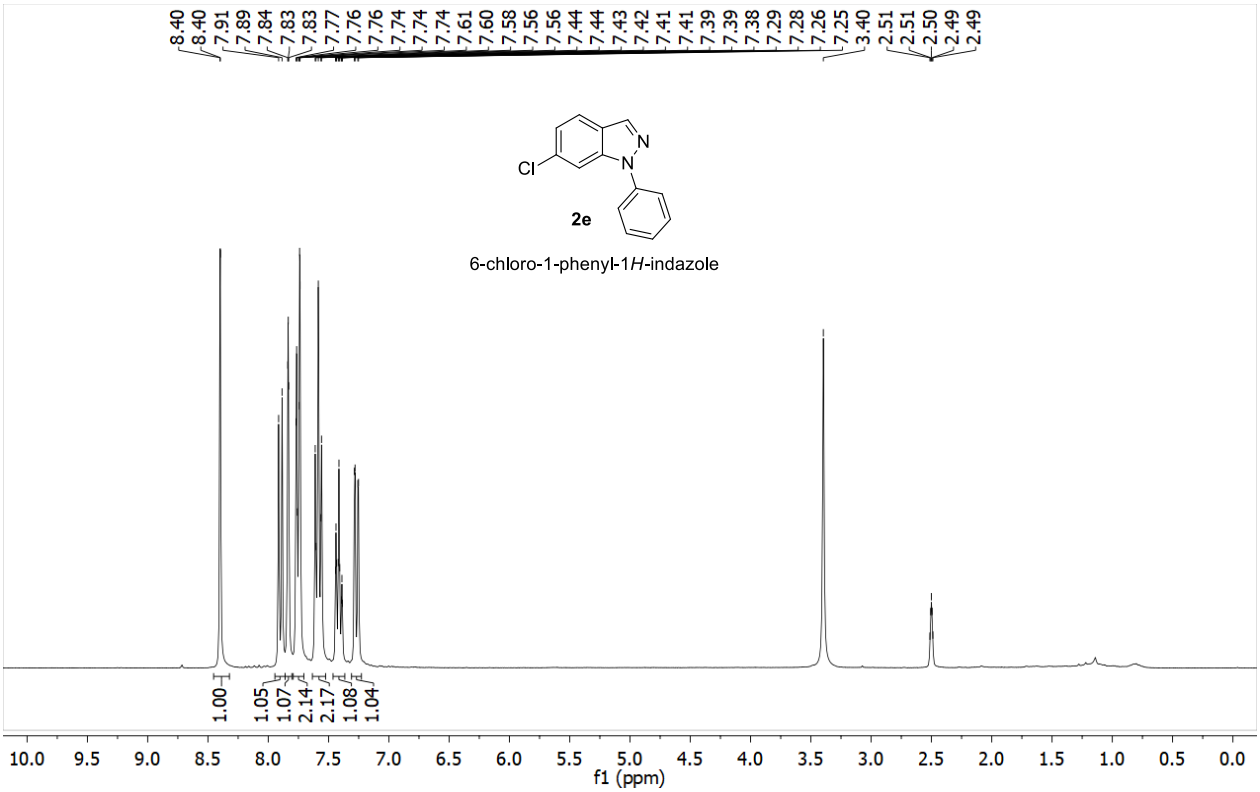


Figure S23. ^{1}H NMR spectrum of compound **2e** (300 MHz, DMSO-d_6).

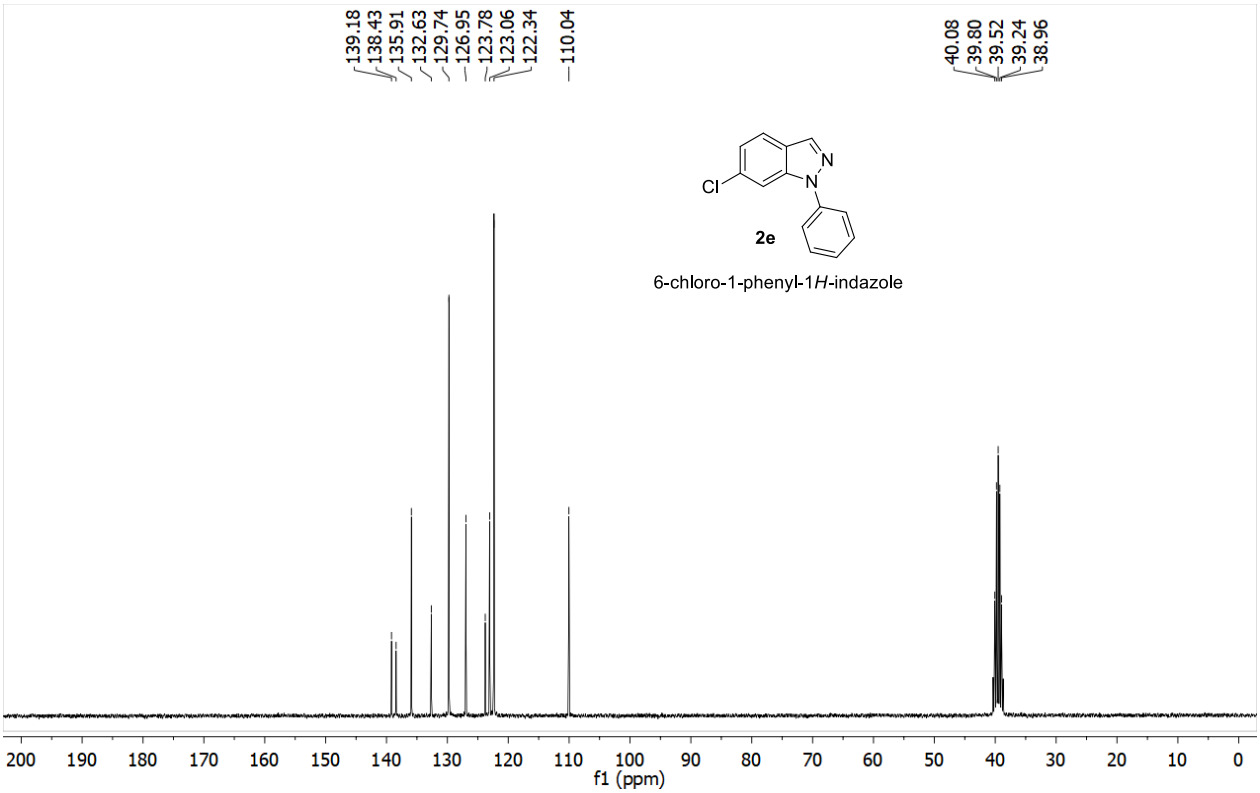


Figure S24. ^{13}C NMR spectrum of compound **2e** (75 MHz, DMSO-d_6).

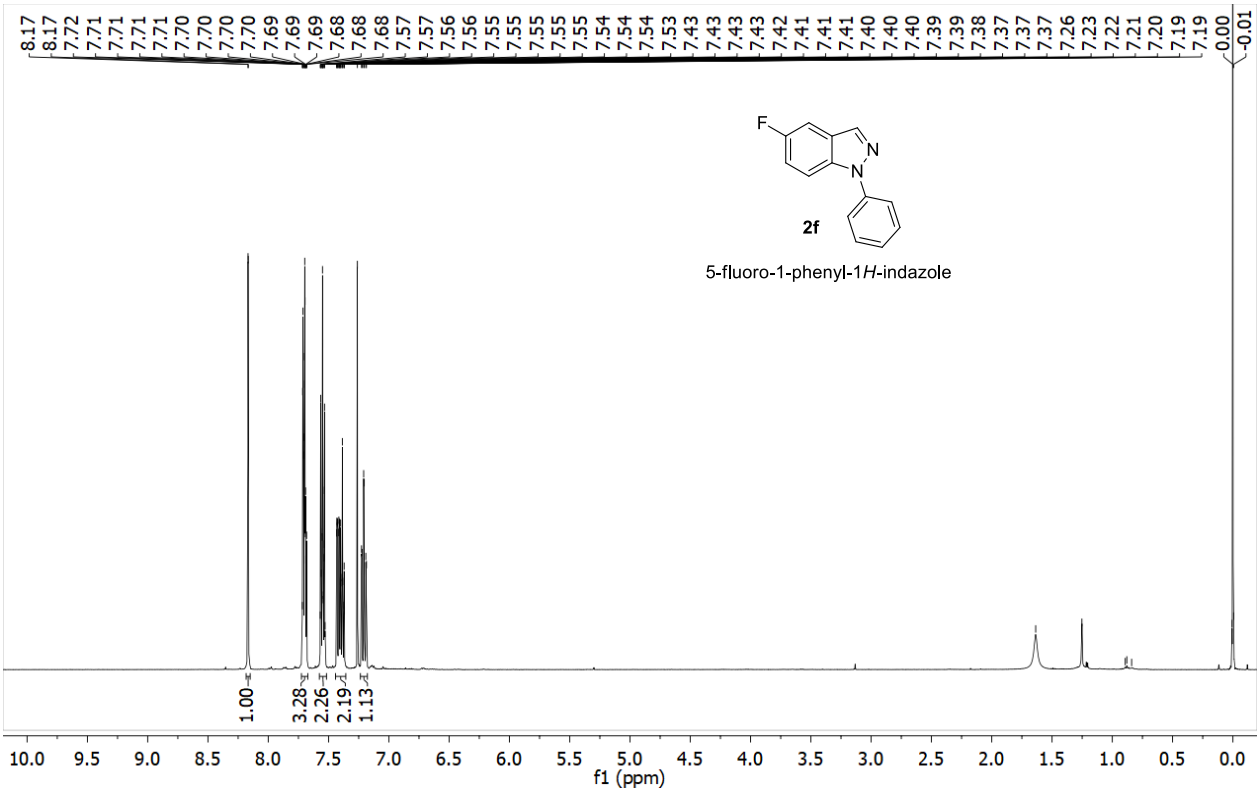


Figure S25. ^{1}H NMR spectrum of compound **2f** (500 MHz, $CDCl_3$).

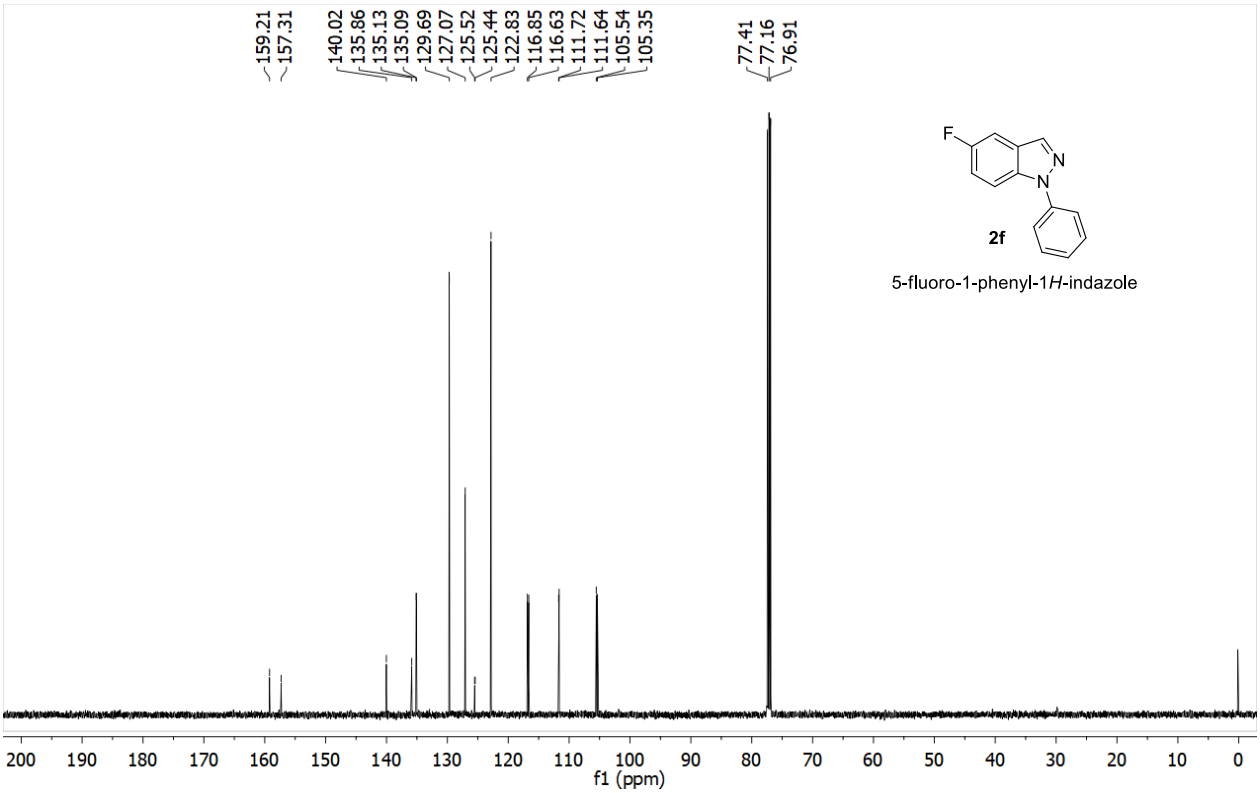


Figure S26. ^{13}C NMR spectrum of compound **2f** (125 MHz, $CDCl_3$).

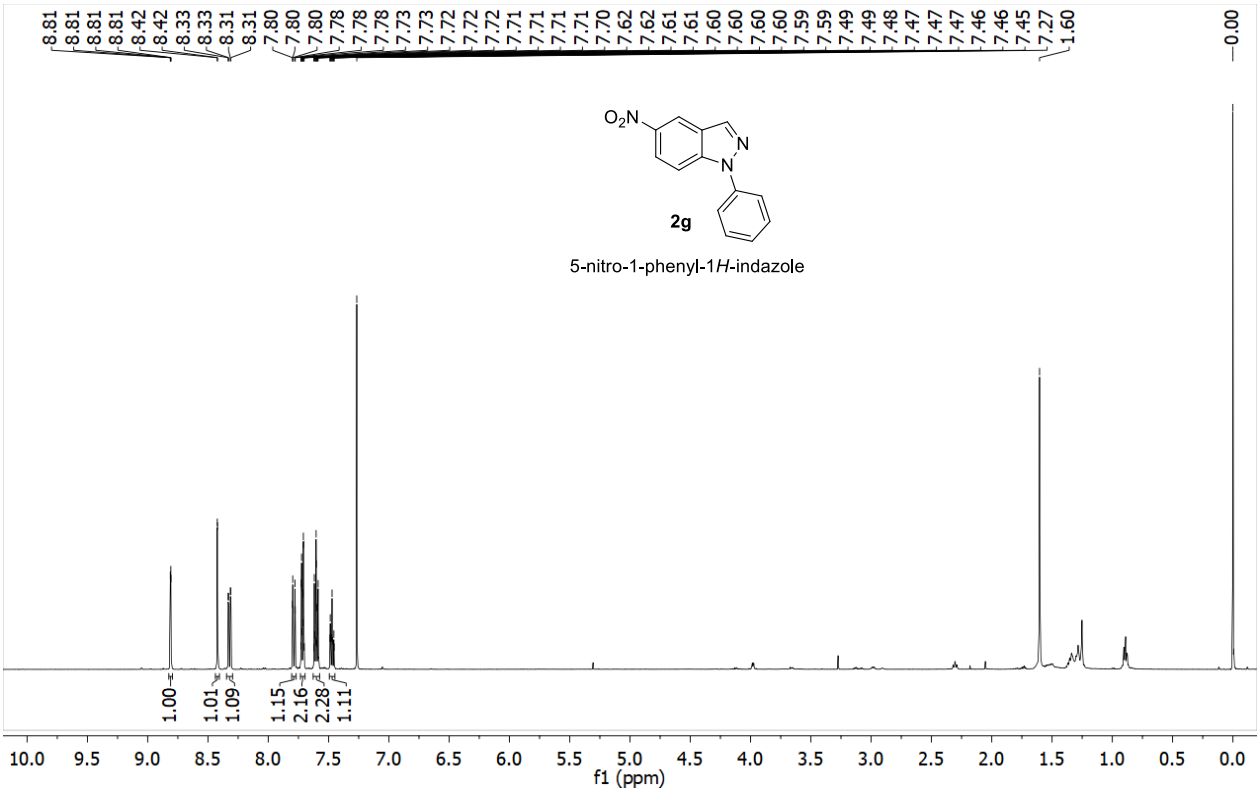


Figure S27. ^{1}H NMR spectrum of compound **2g** (500 MHz, $CDCl_3$).

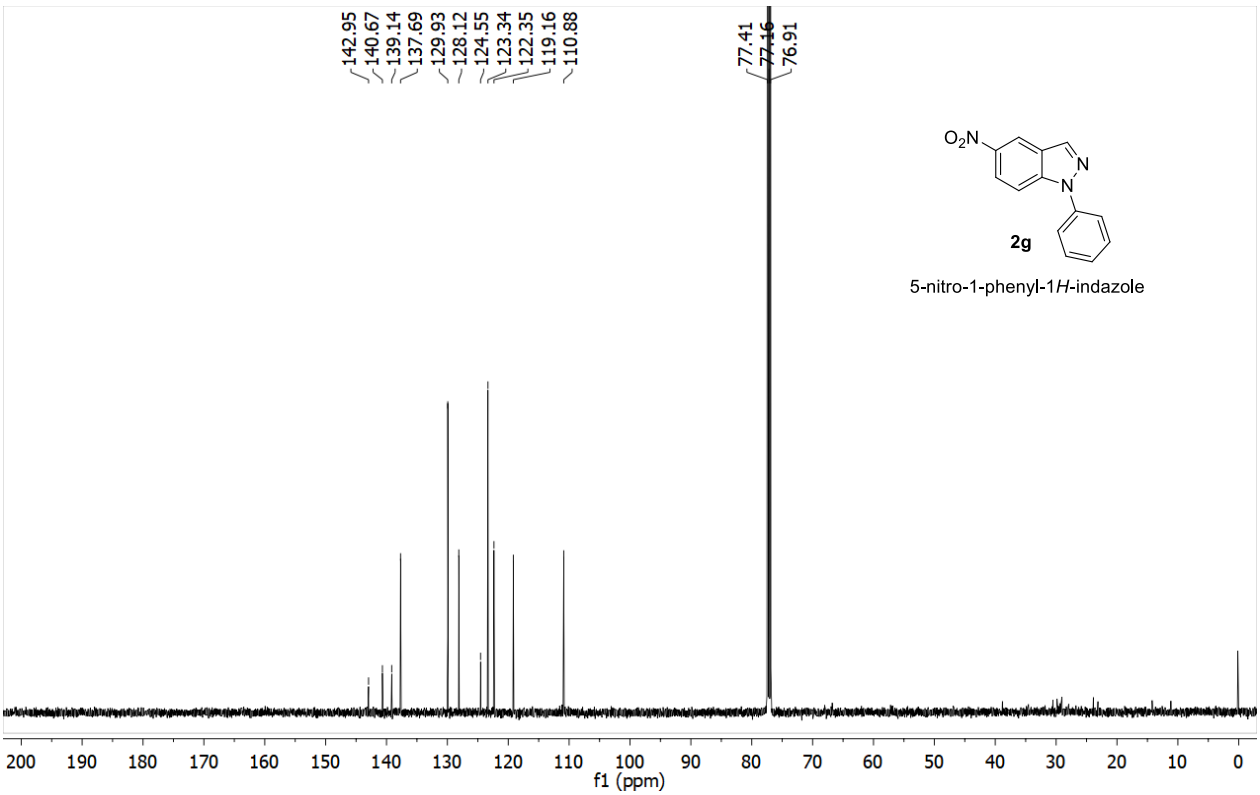


Figure S28. ^{13}C NMR spectrum of compound **2g** (125 MHz, $CDCl_3$).

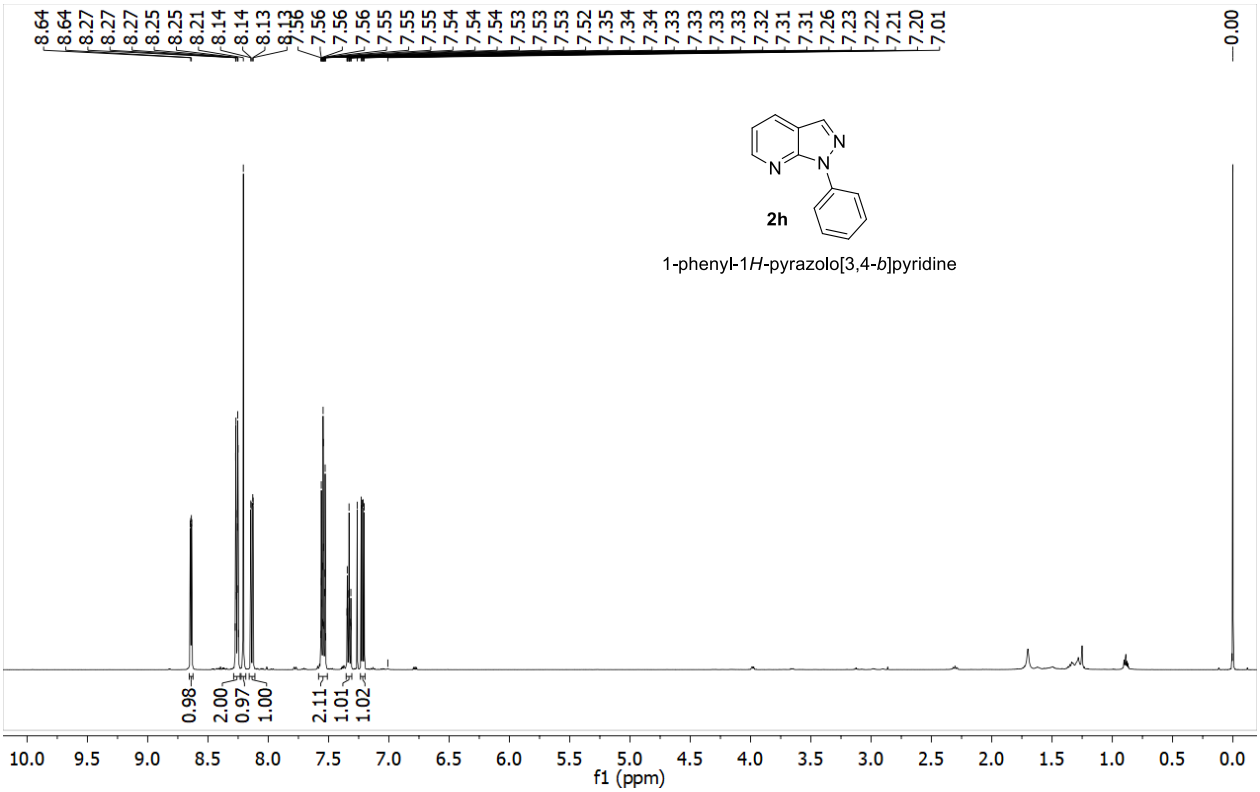


Figure S29. ^{1}H NMR spectrum of compound **2h** (500 MHz, $CDCl_3$).

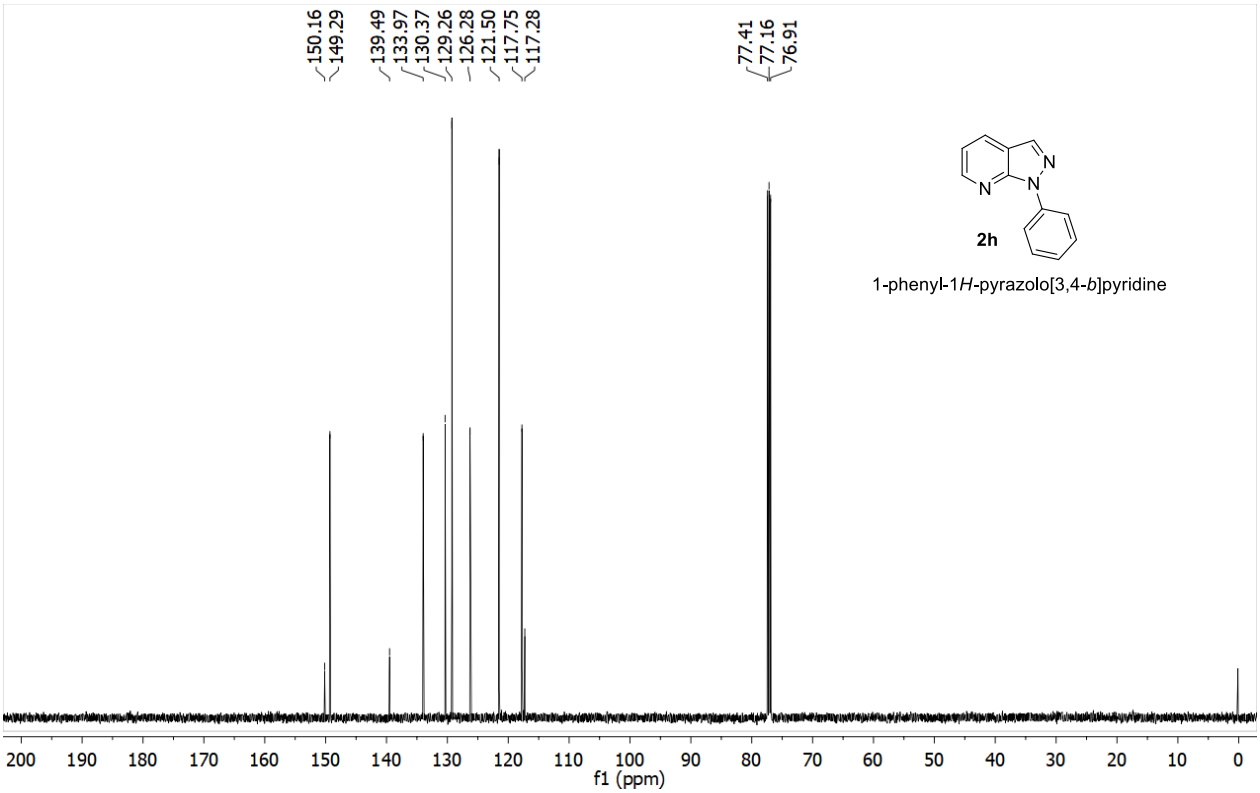


Figure S30. ^{13}C NMR spectrum of compound **2h** (125 MHz, $CDCl_3$).

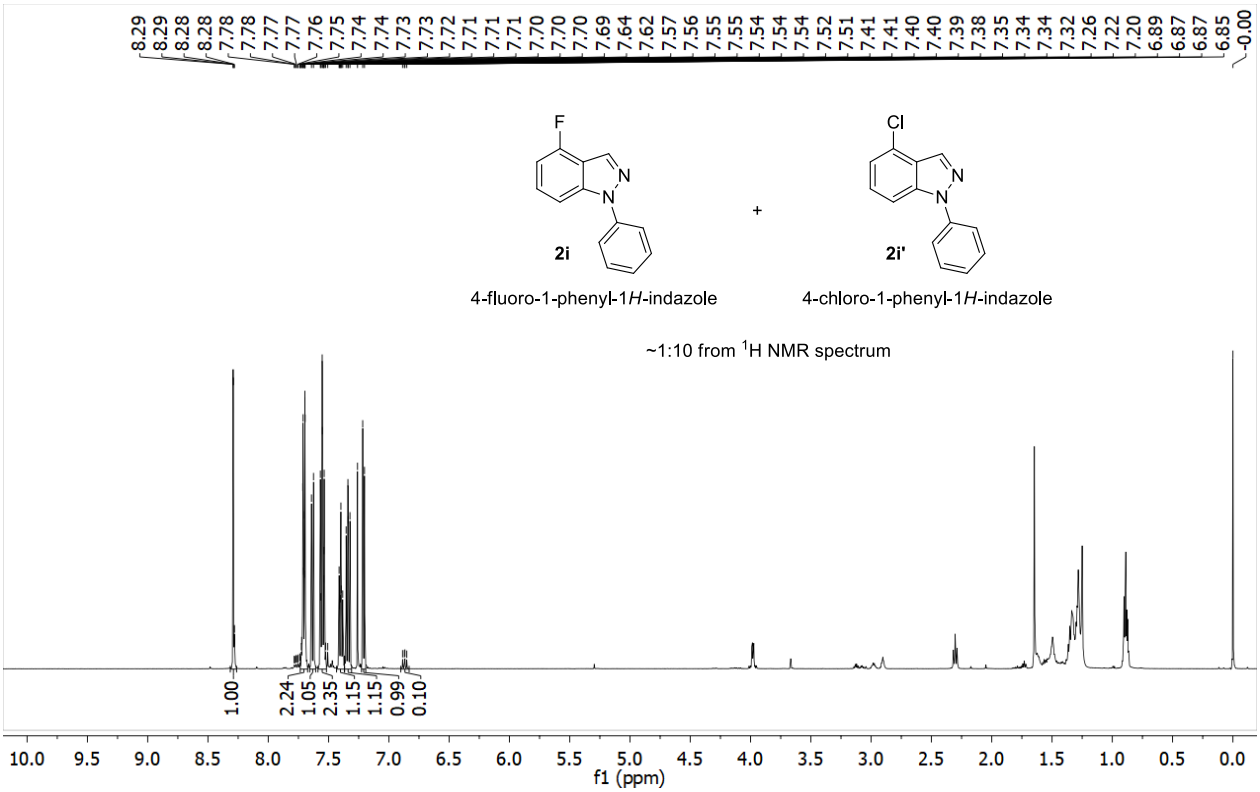


Figure S31. ^{1}H NMR spectrum of the mixture of compound **2i** and **2i'** (500 MHz, $CDCl_3$).

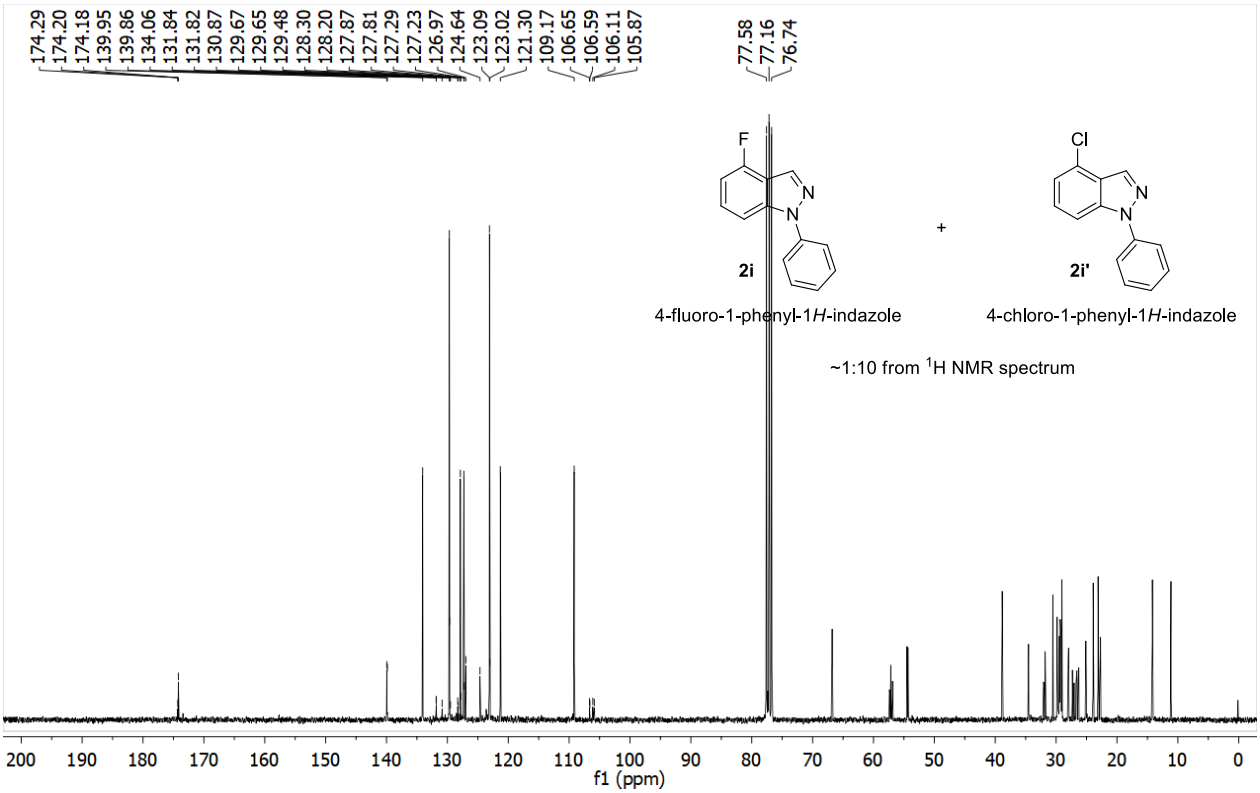


Figure S32. ^{13}C NMR spectrum of the mixture of compound **2i** and **2i'** (125 MHz, $CDCl_3$).

^{1}H and ^{13}C NMR spectra of *N*-thiazolyl-1*H*-indazoles

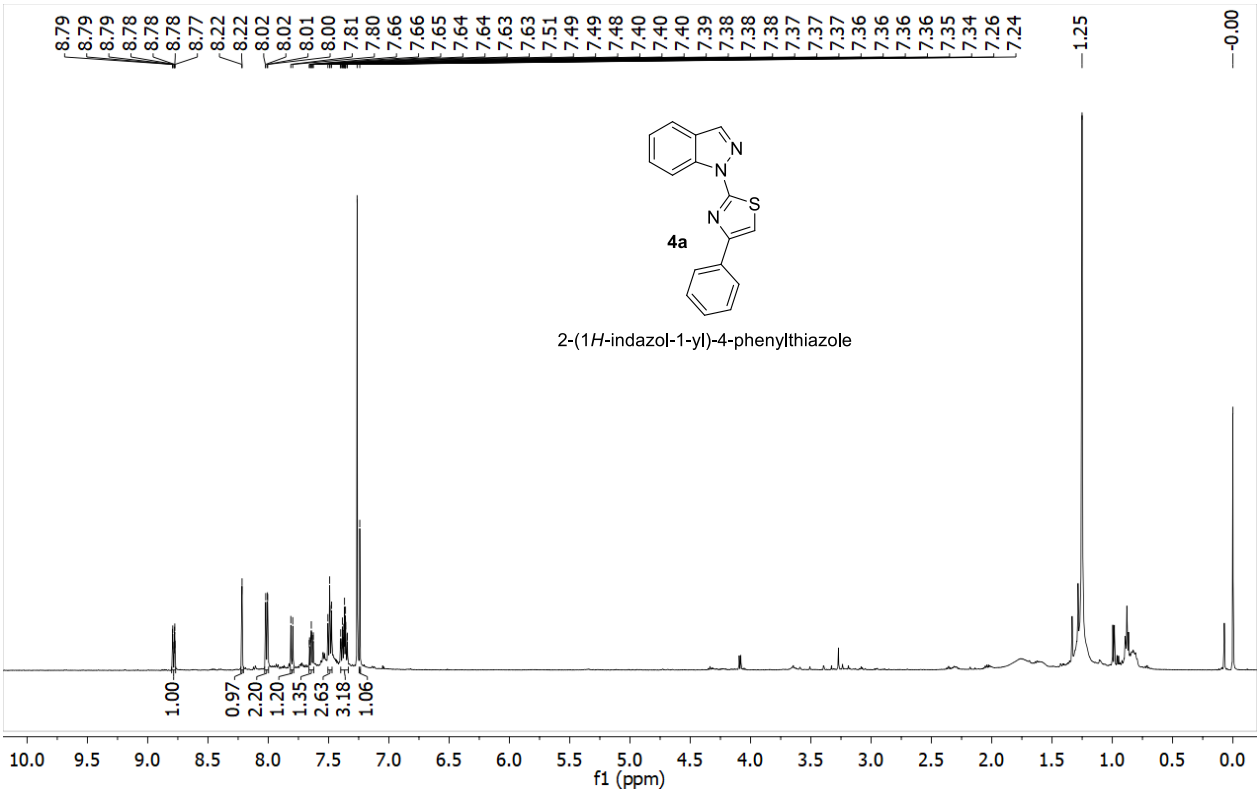


Figure S33. ^{1}H NMR spectrum of compound **4a** (500 MHz, $CDCl_3$).

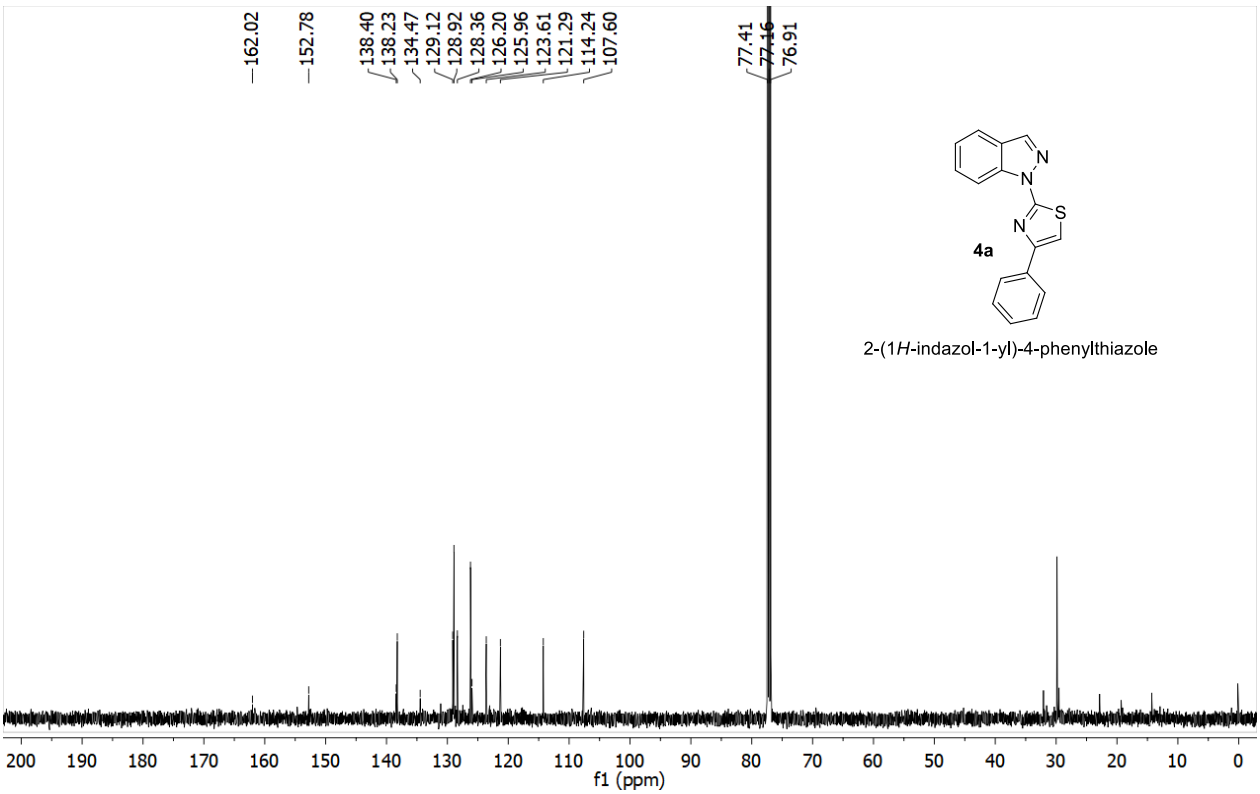


Figure S34. ^{13}C NMR spectrum of compound **4a** (125 MHz, $CDCl_3$).

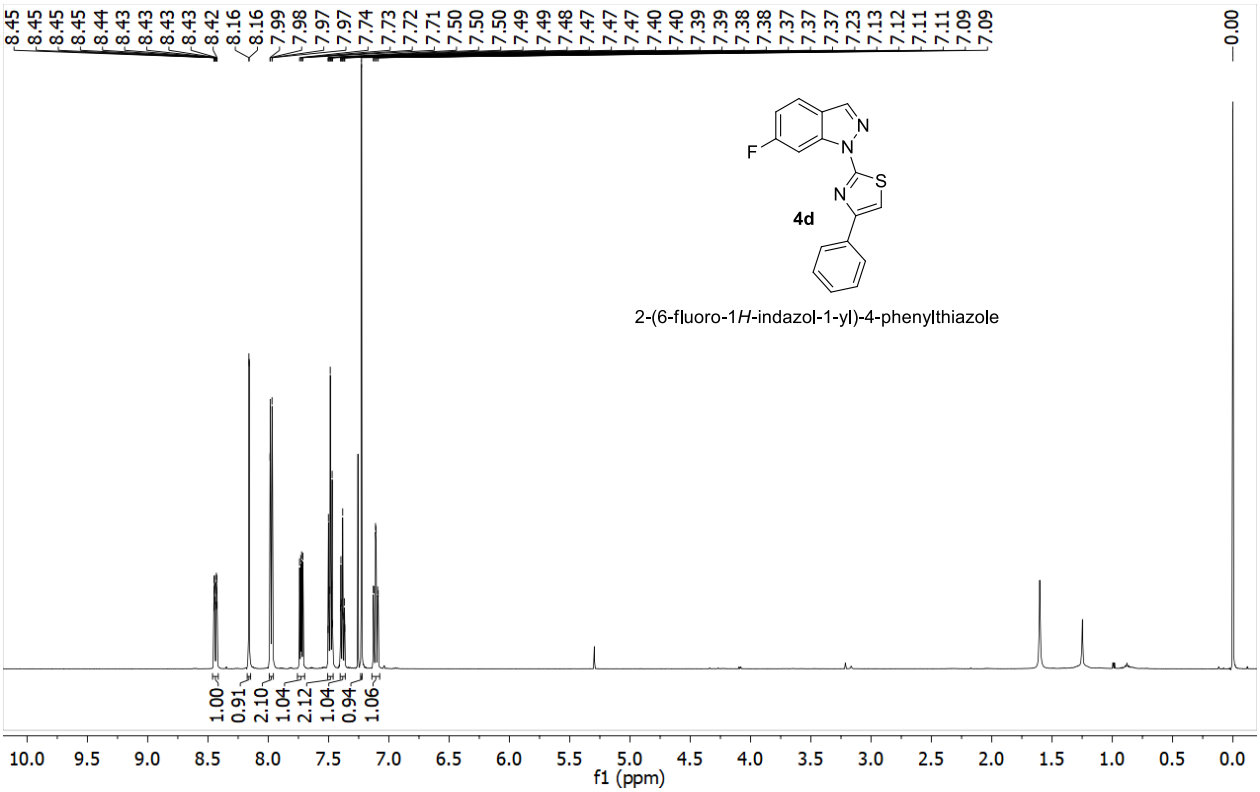


Figure S35. ^{1}H NMR spectrum of compound **4d** (500 MHz, $CDCl_3$).

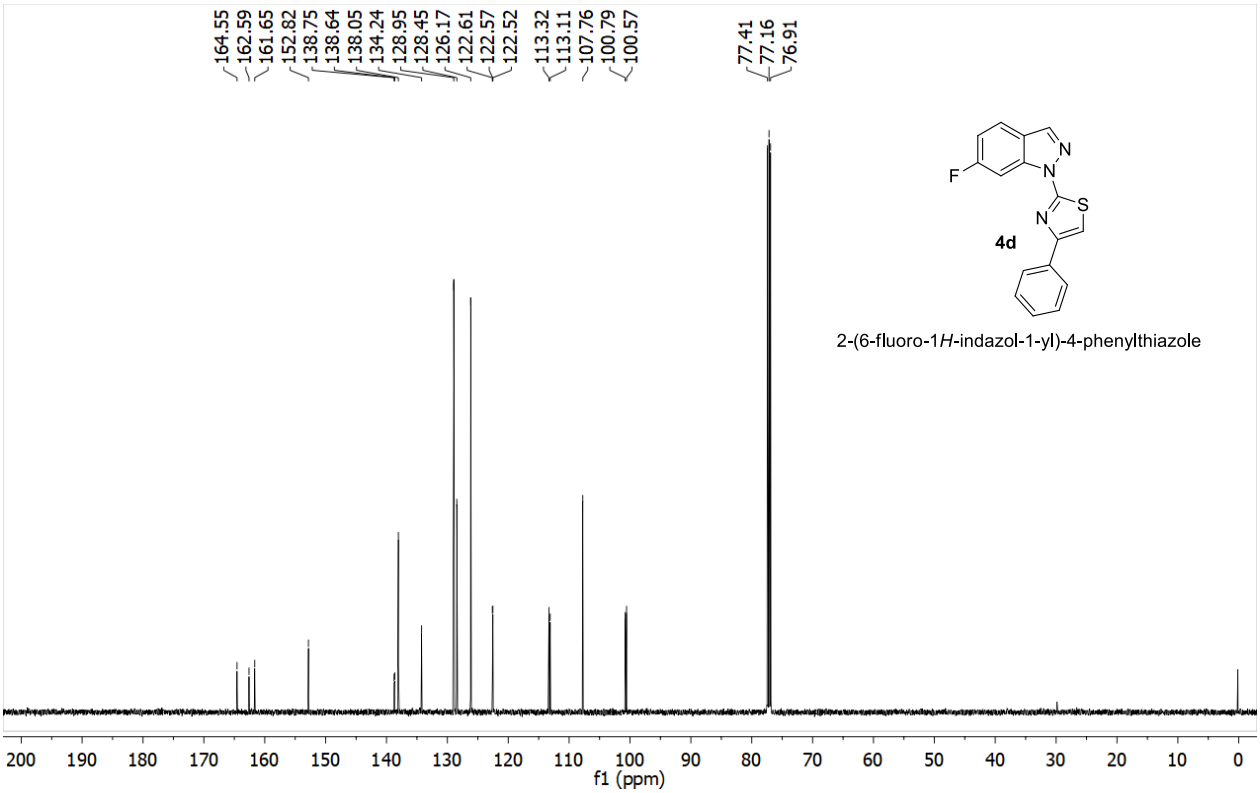


Figure S36. ^{13}C NMR spectrum of compound **4d** (125 MHz, $CDCl_3$).

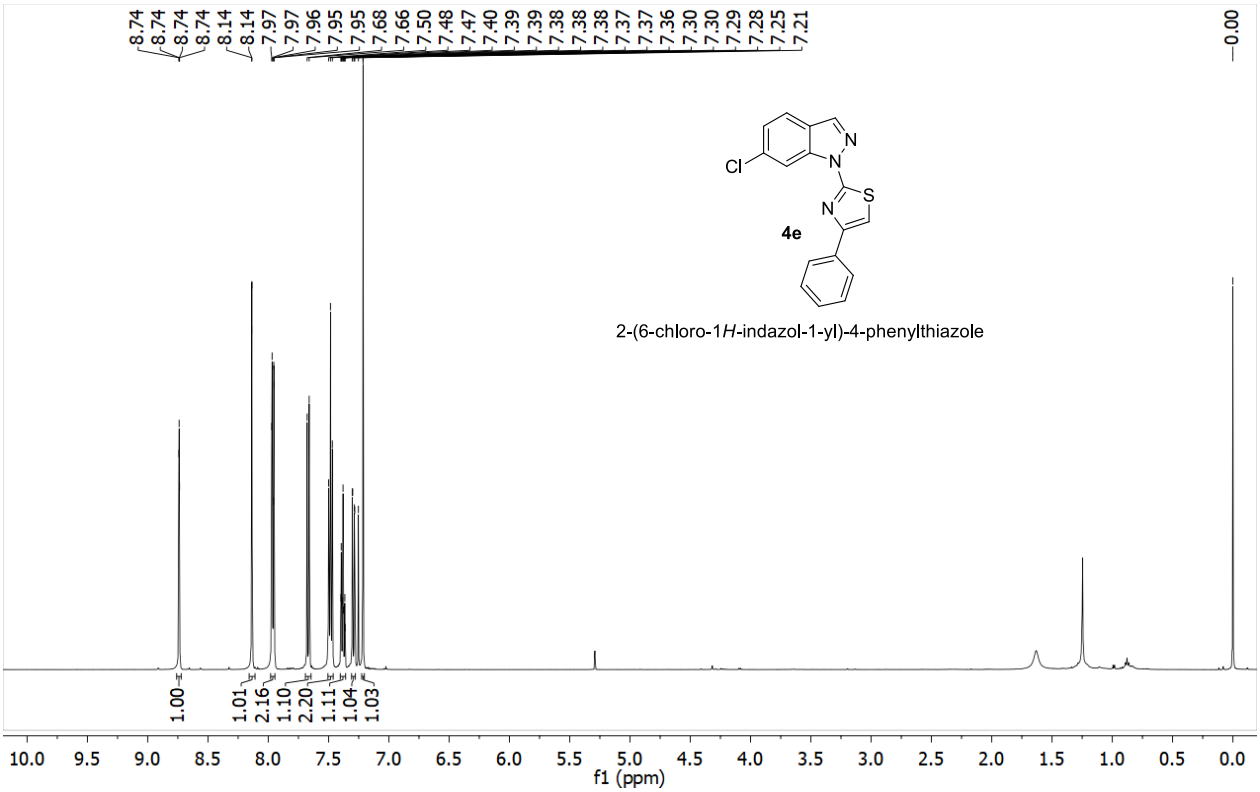


Figure S37. ^{1}H NMR spectrum of compound **4e** (500 MHz, $CDCl_3$).

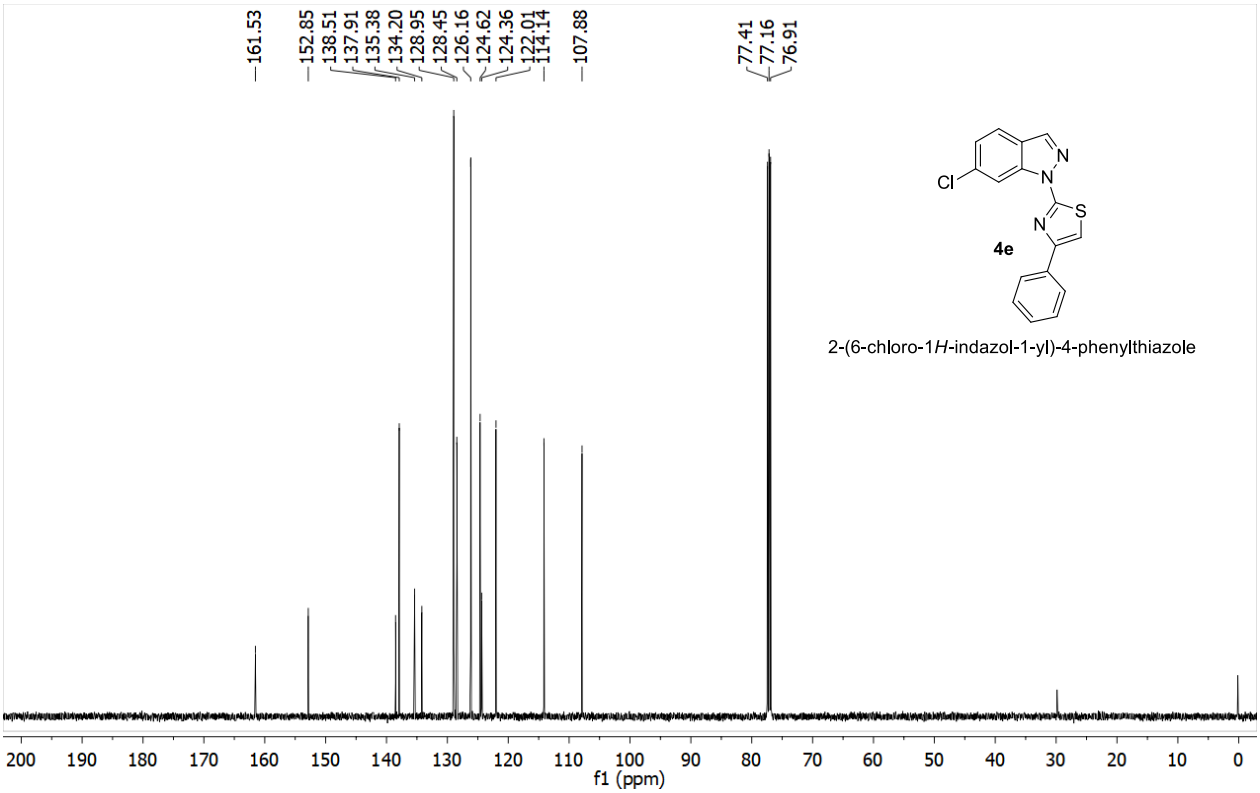


Figure S38. ^{13}C NMR spectrum of compound **4e** (125 MHz, $CDCl_3$).

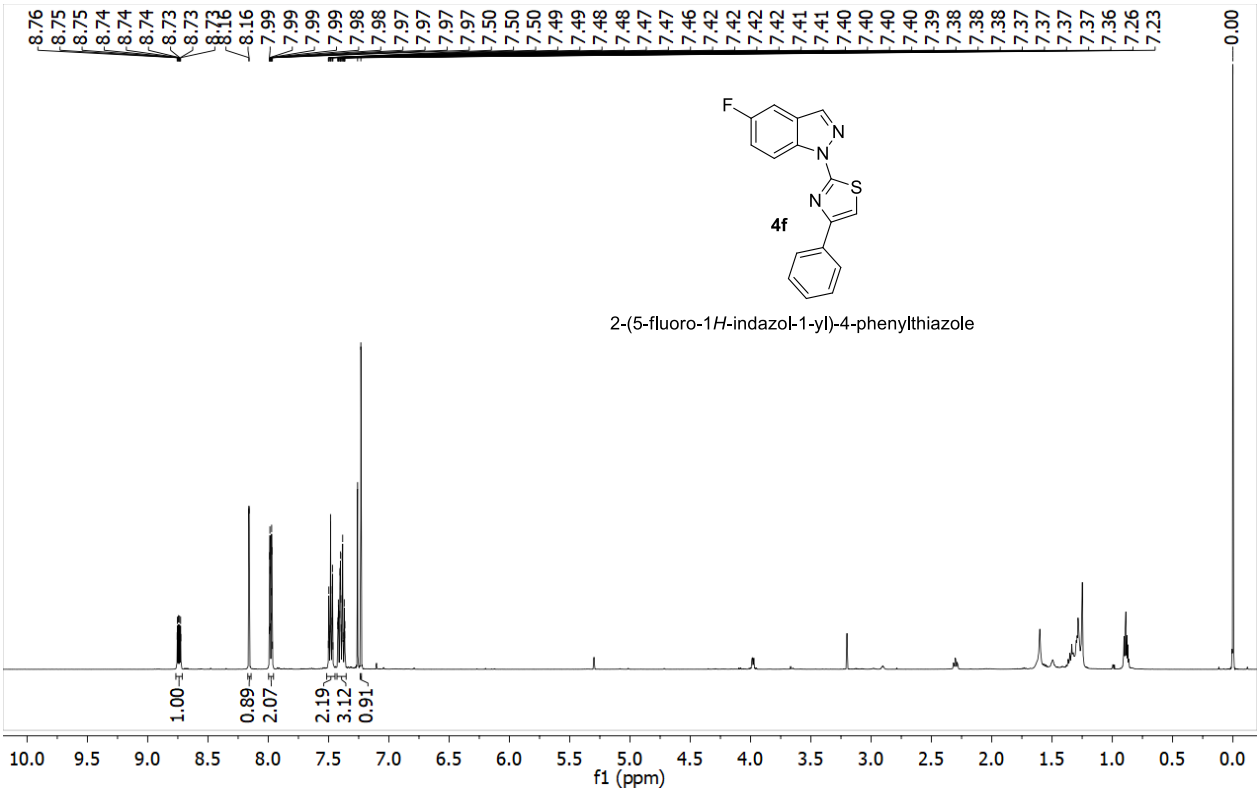


Figure S39. ^{1}H NMR spectrum of compound **4f** (500 MHz, $CDCl_3$).

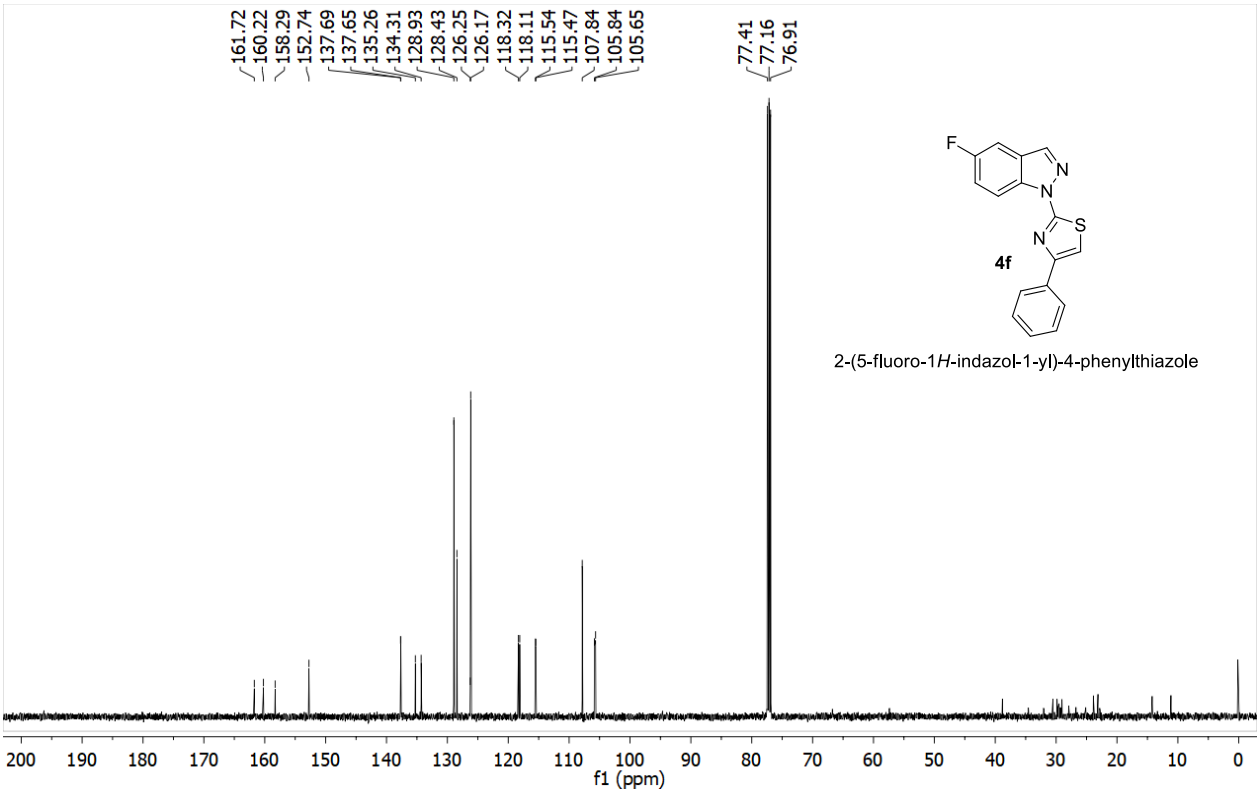


Figure S40. ^{13}C NMR spectrum of compound **4f** (125 MHz, $CDCl_3$).

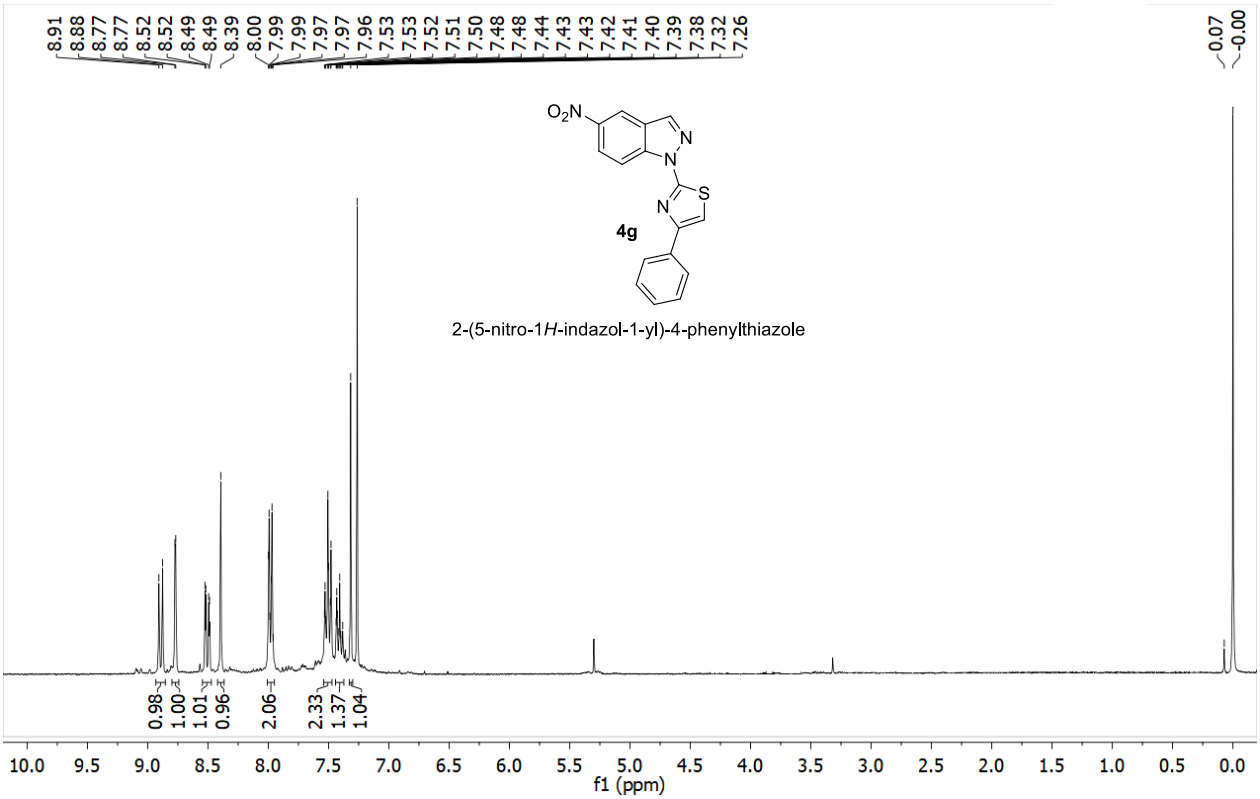


Figure S41. ^{1}H NMR spectrum of compound **4g** (300 MHz, $CDCl_3$).

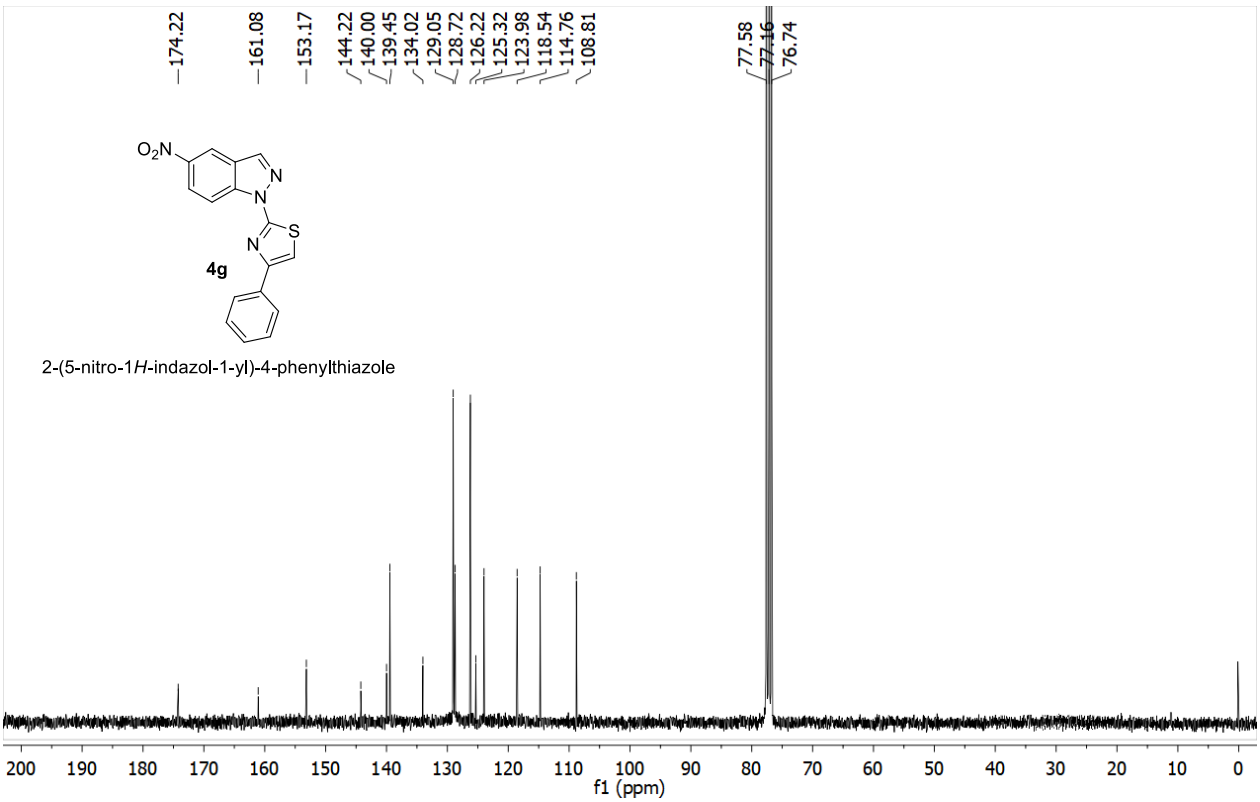


Figure S42. ^{13}C NMR spectrum of compound **4g** (75 MHz, $CDCl_3$).

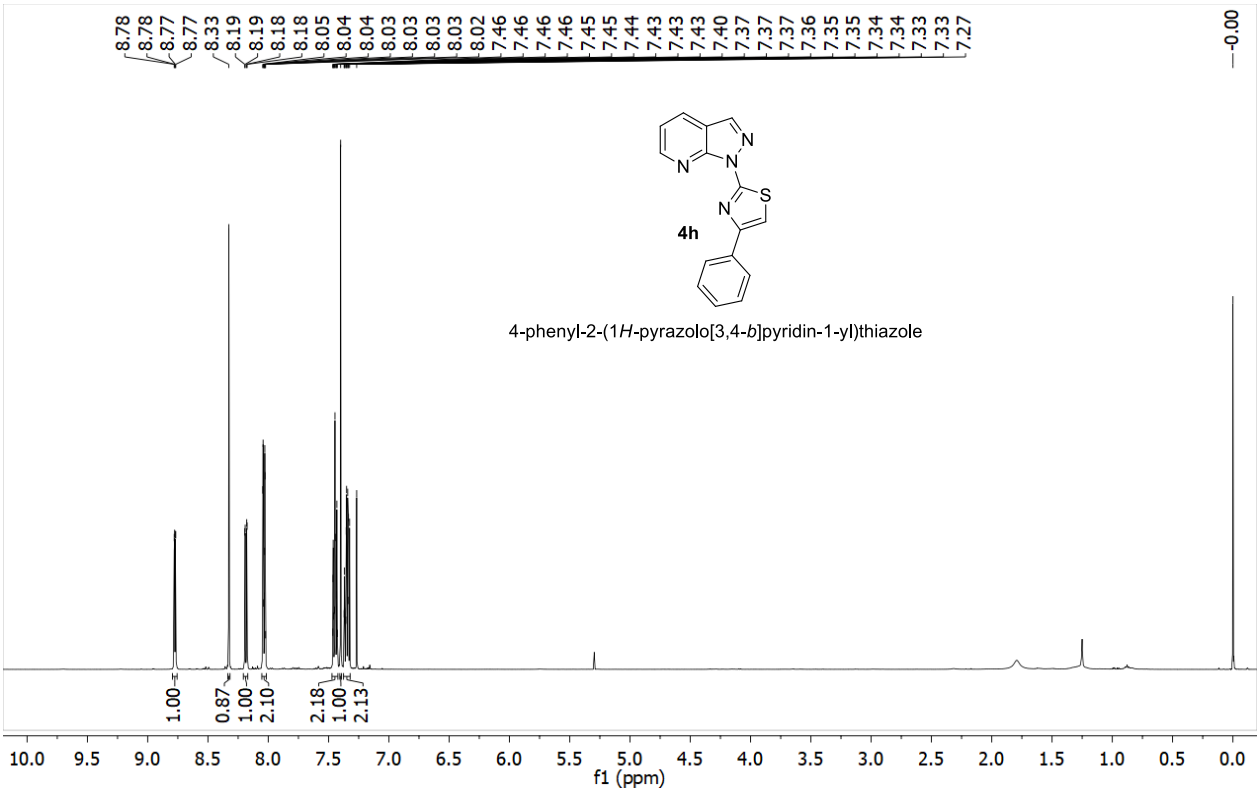


Figure S43. ^{1}H NMR spectrum of compound **4h** (500 MHz, $CDCl_3$).

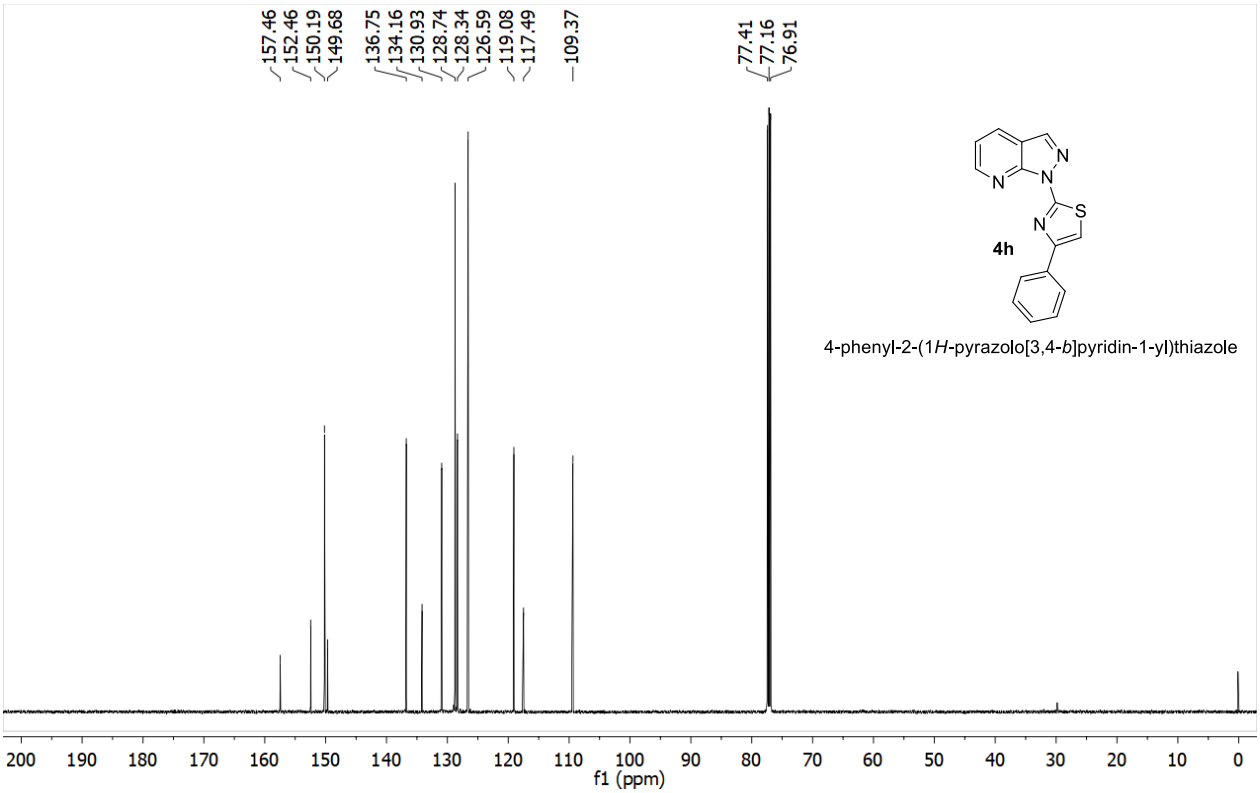


Figure S44. ^{13}C NMR spectrum of compound **4h** (125 MHz, $CDCl_3$).

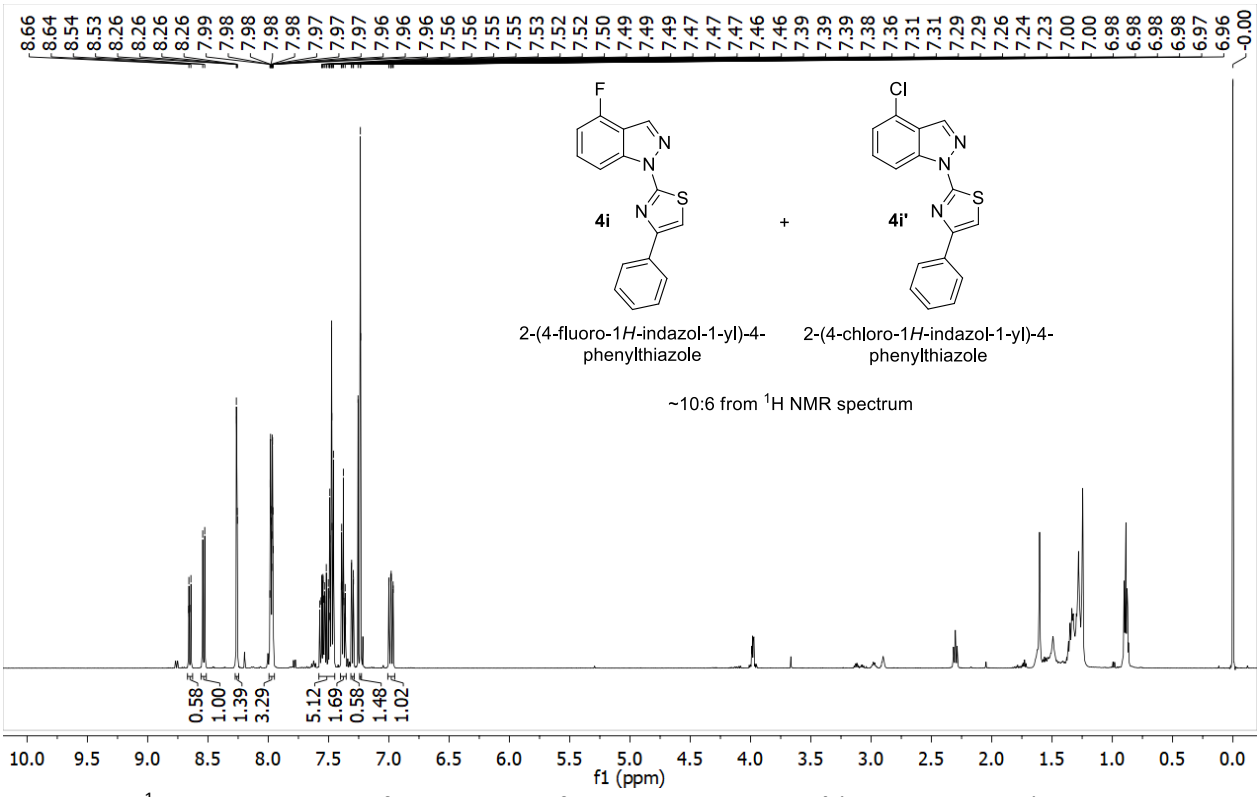


Figure S45. ^{1}H NMR spectrum of the mixture of compounds **4i** and **4i'** (500 MHz, $CDCl_3$).

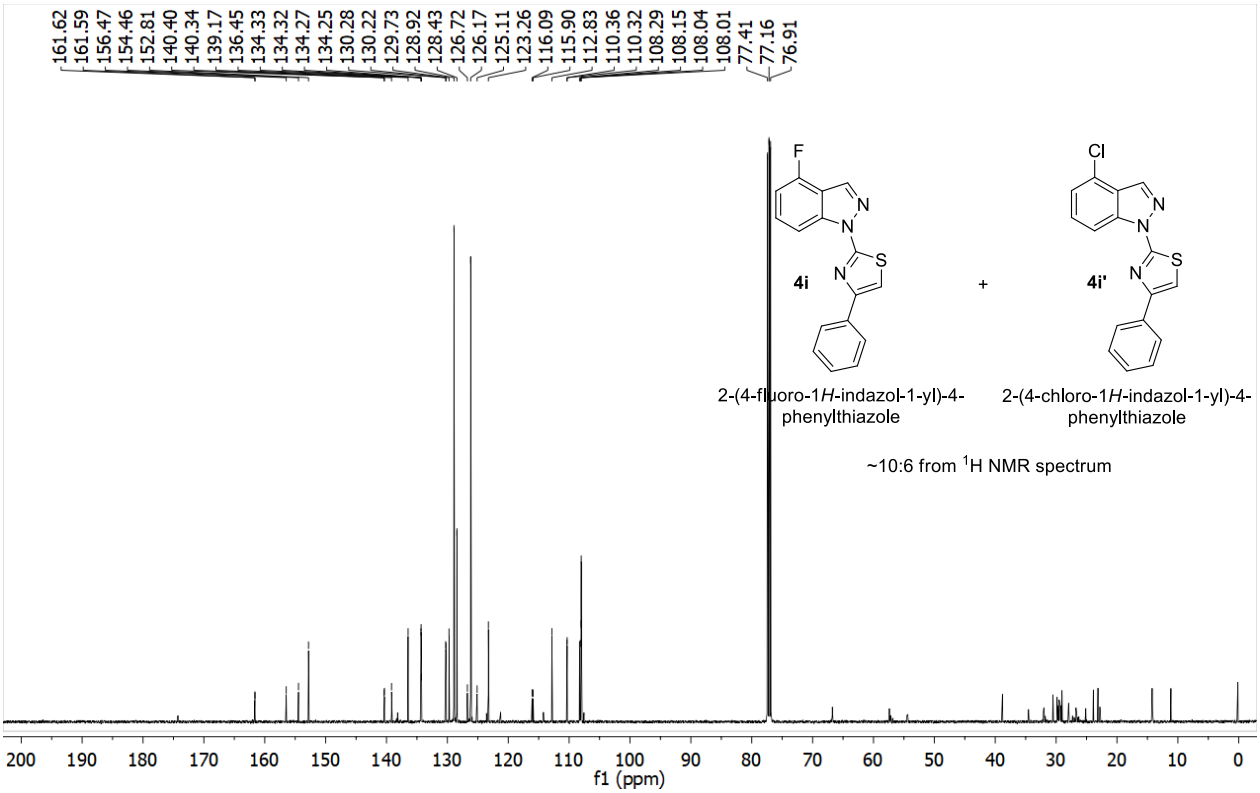


Figure S46. ^{13}C NMR spectrum of the mixture of compounds **4i** and **4i'** (175 MHz, $CDCl_3$).

HRMS spectra of *N*-phenylhydrazones 1a–i

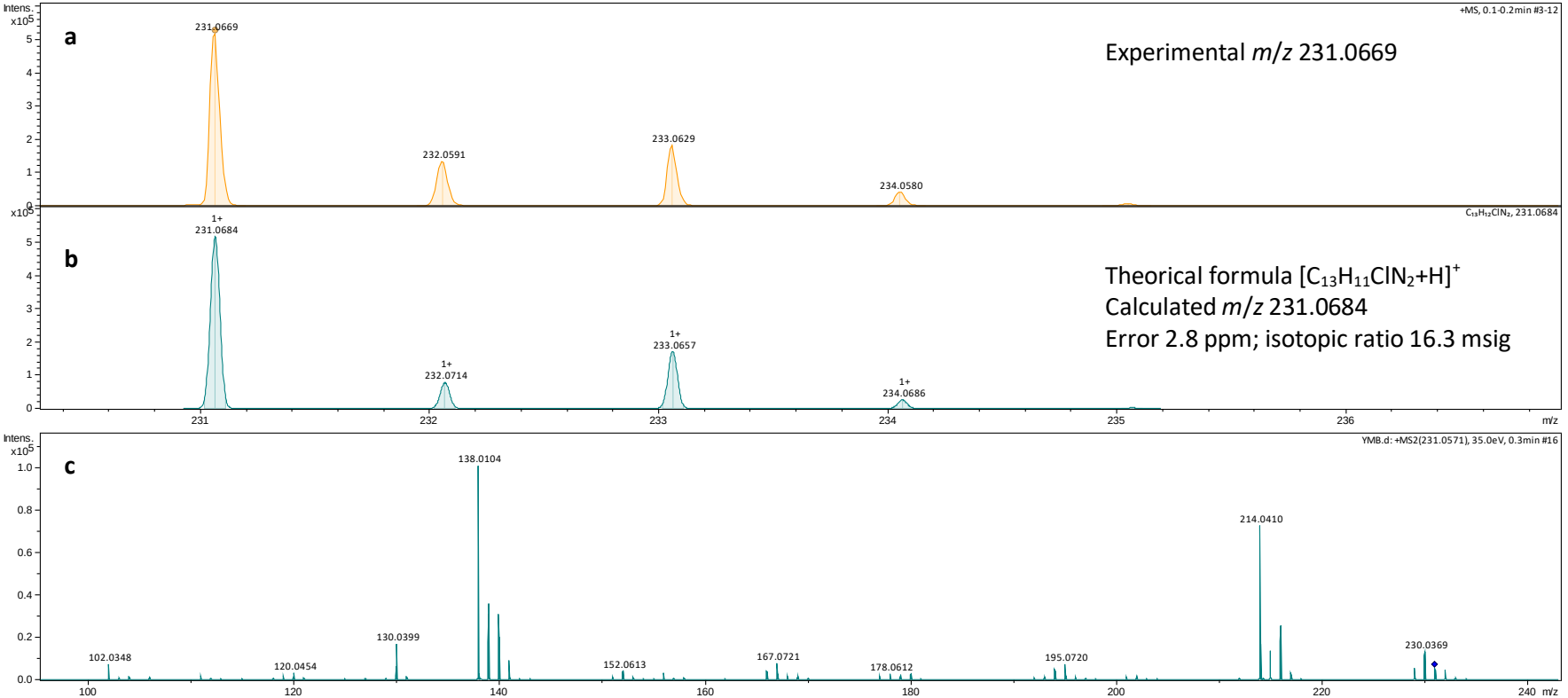


Figure S47. The HRMS analysis of compound **1a**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 230.3 and 236.9 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

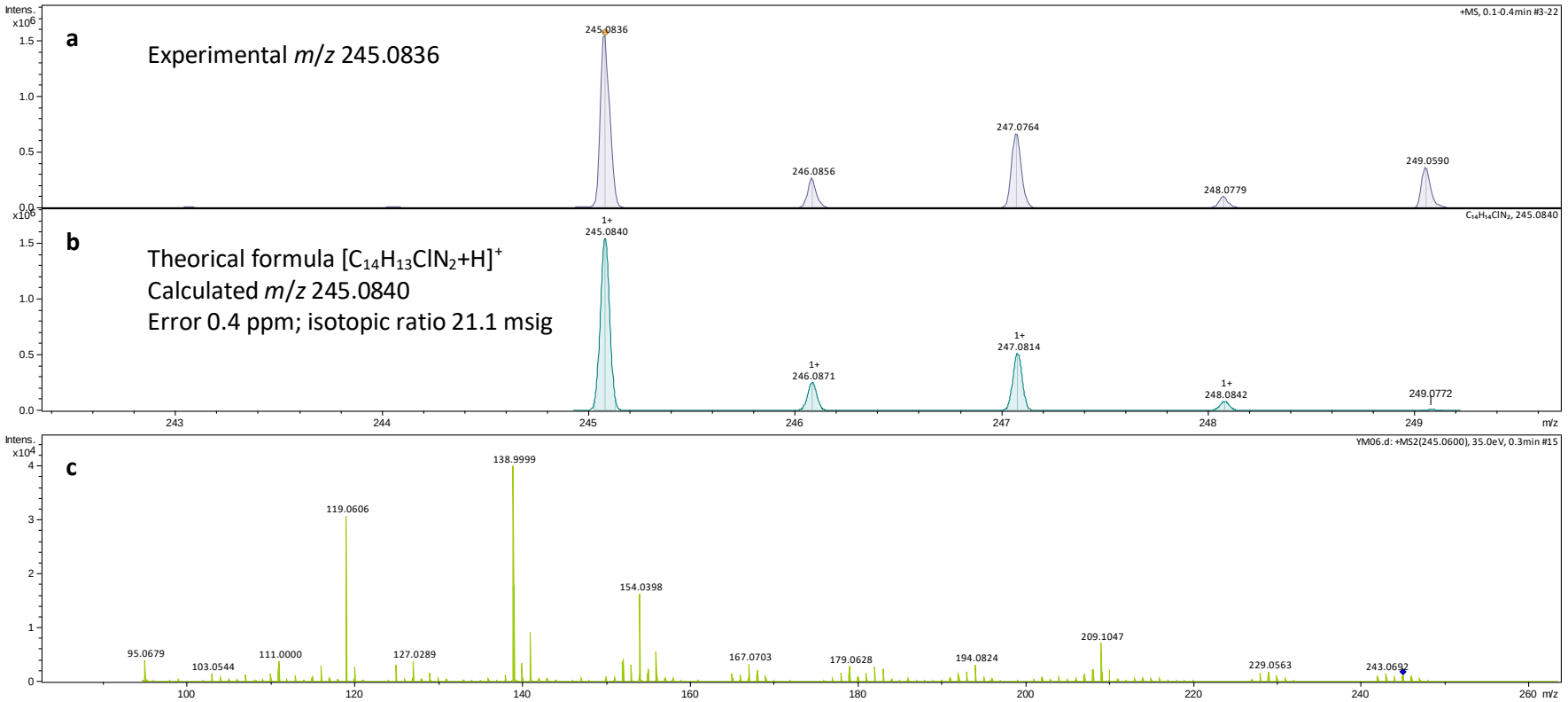


Figure S48. The HRMS analysis of compound **1b**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 242.4 and 249.7 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

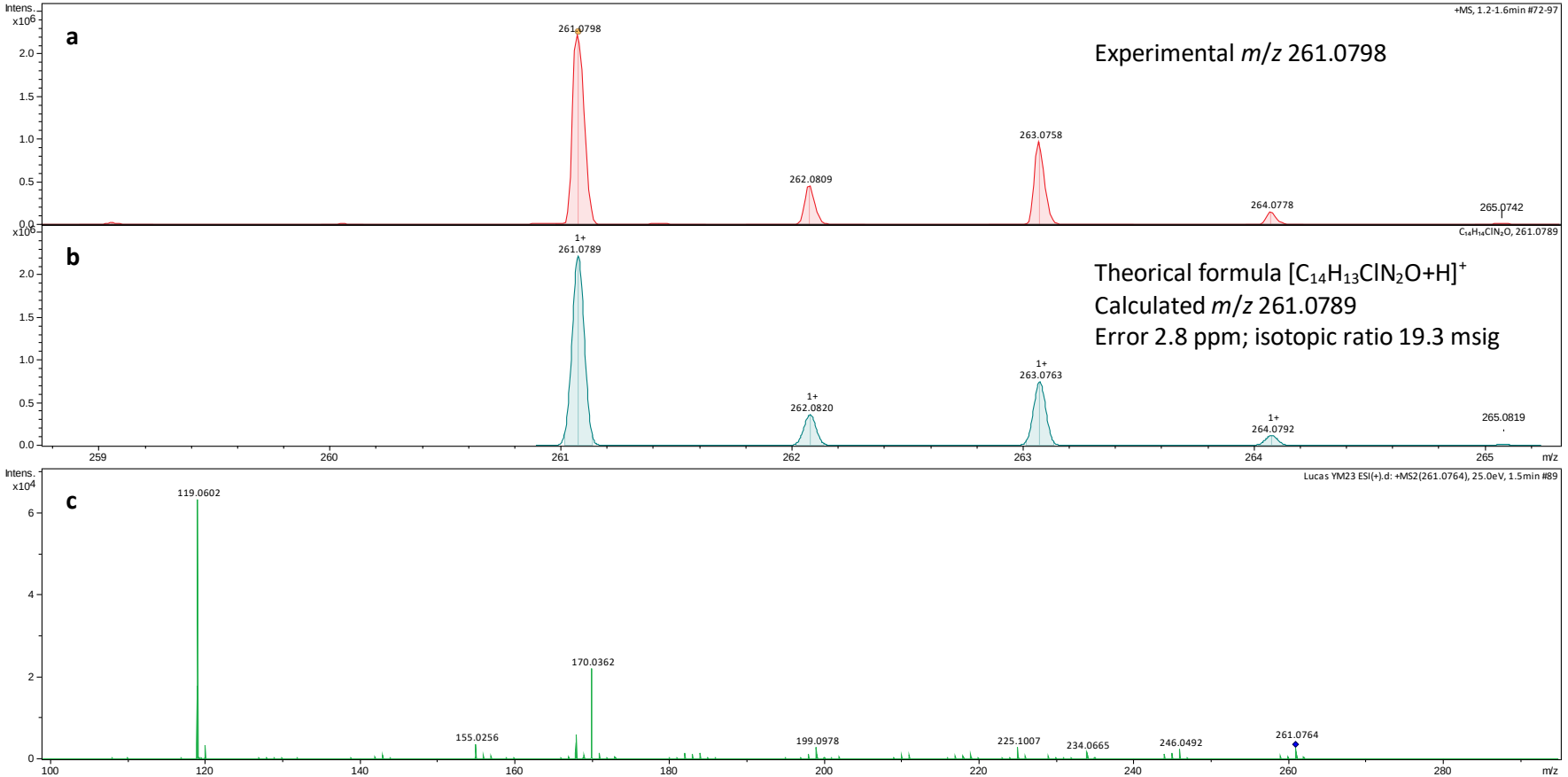


Figure S49. The HRMS analysis of compound **1c**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 242.4 and 249.7 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

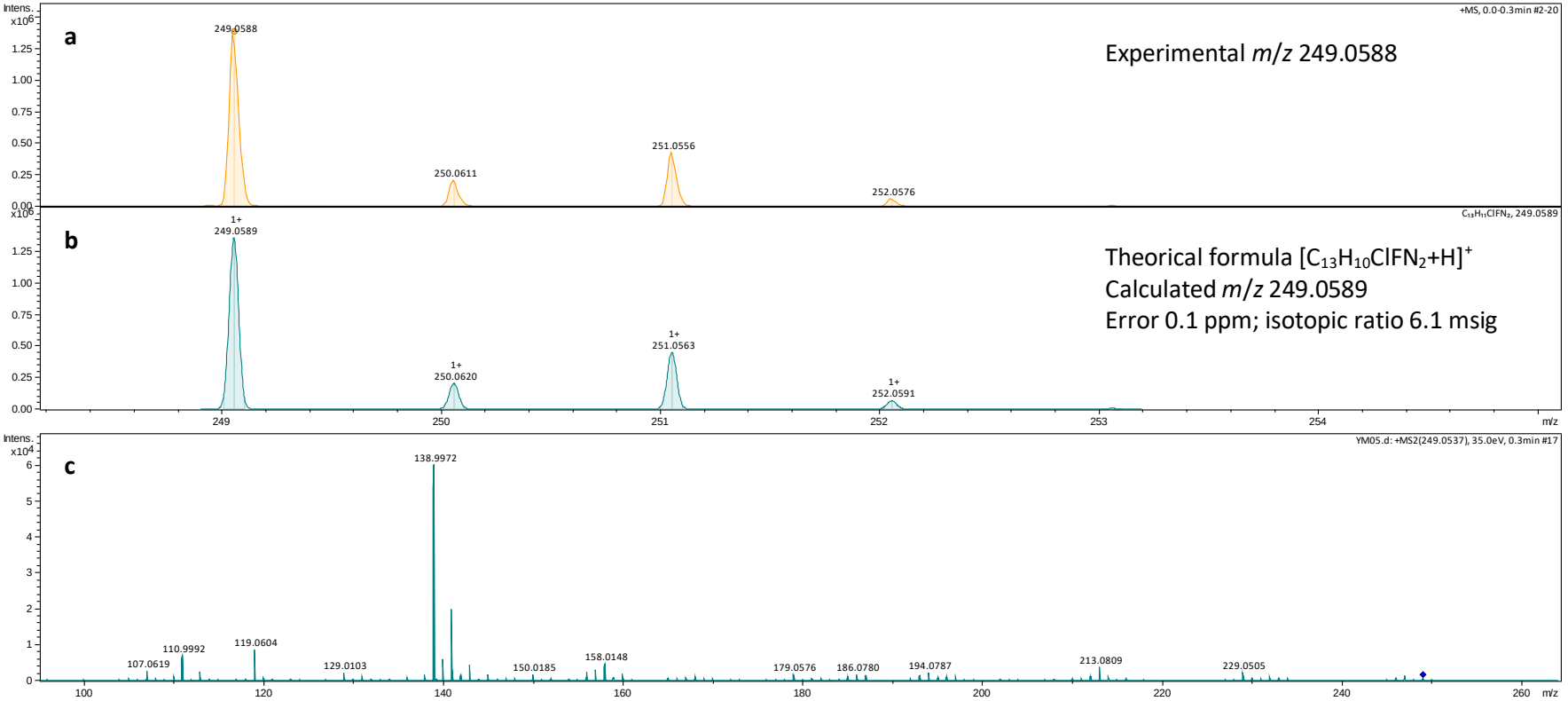


Figure S50. The HRMS analysis of compound **1d**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 248.2 and 255.1 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

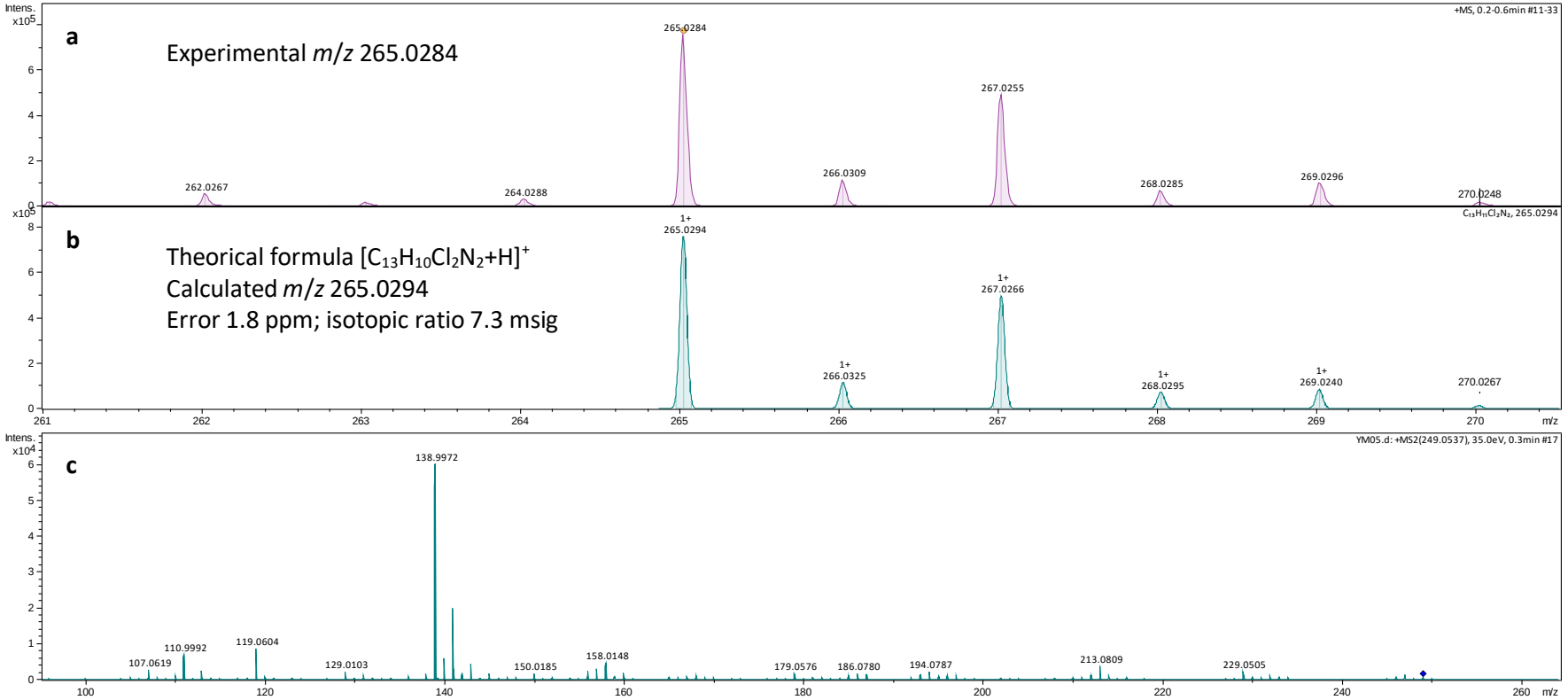


Figure S51. The HRMS analysis of compound **1e**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 261.0 and 270.5 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

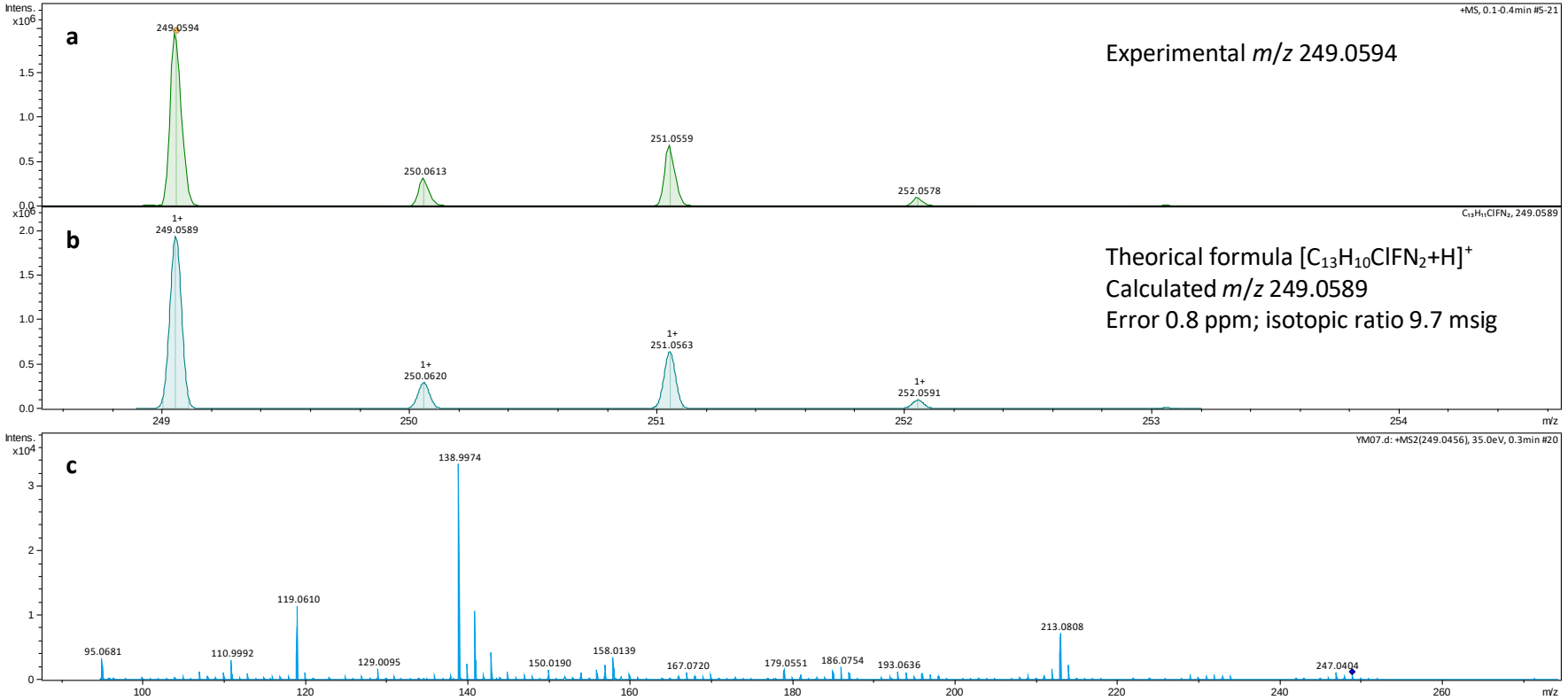


Figure S52. The HRMS analysis of compound **1f**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 248.5 and 254.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

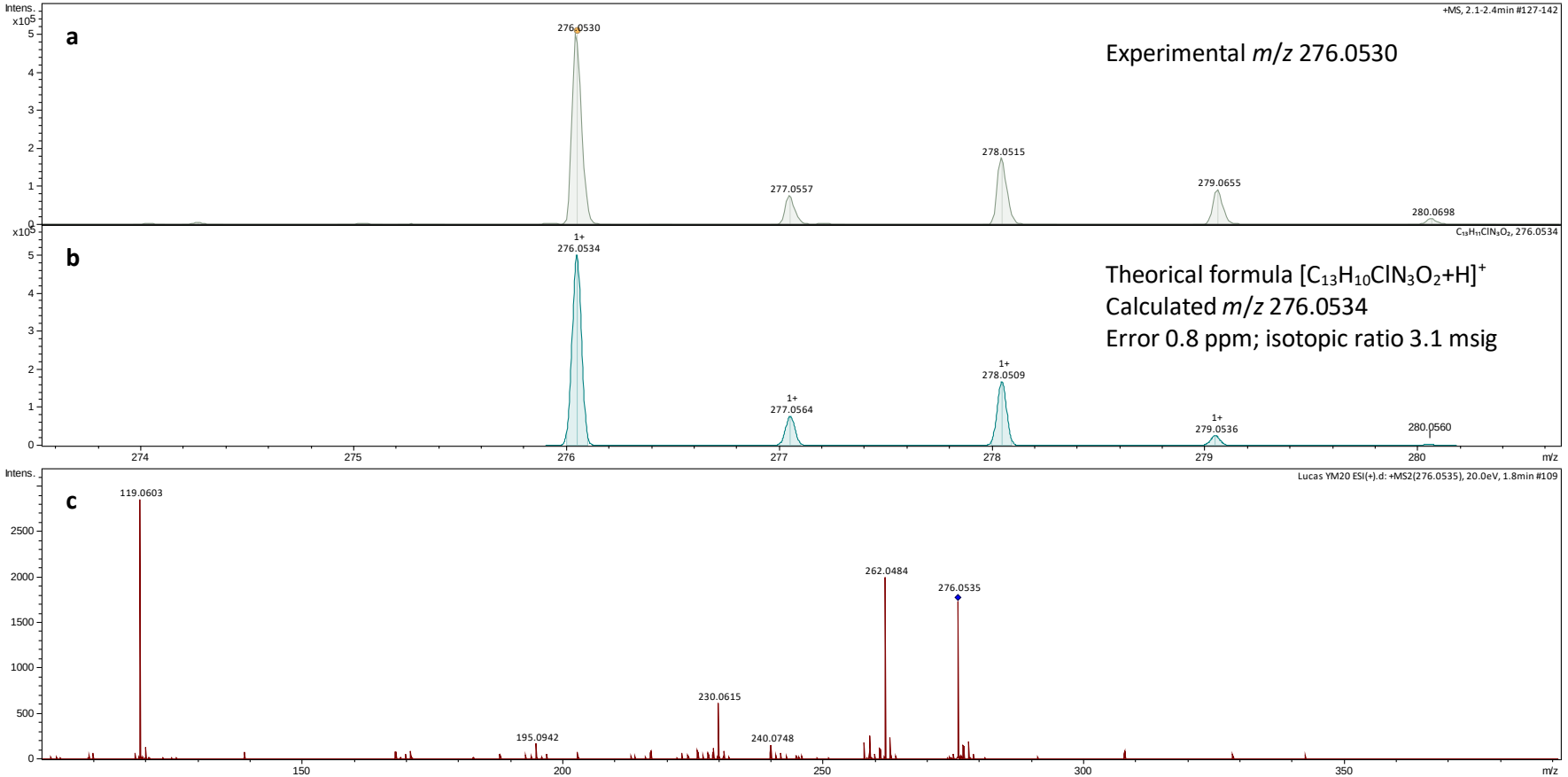


Figure S53. The HRMS analysis of compound **1g**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 248.5 and 254.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

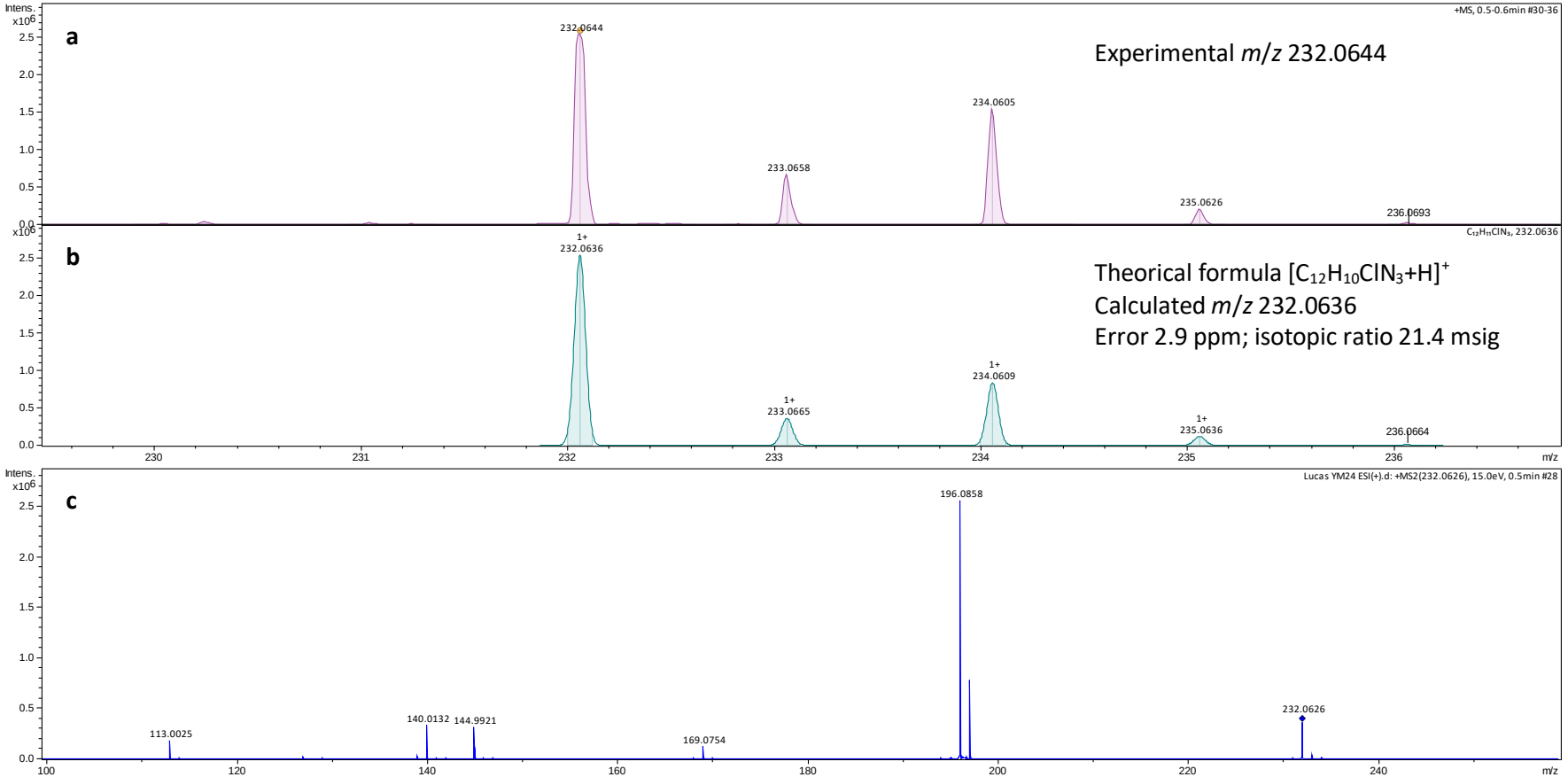


Figure S54. The HRMS analysis of compound **1h**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 229.5 and 236.8 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

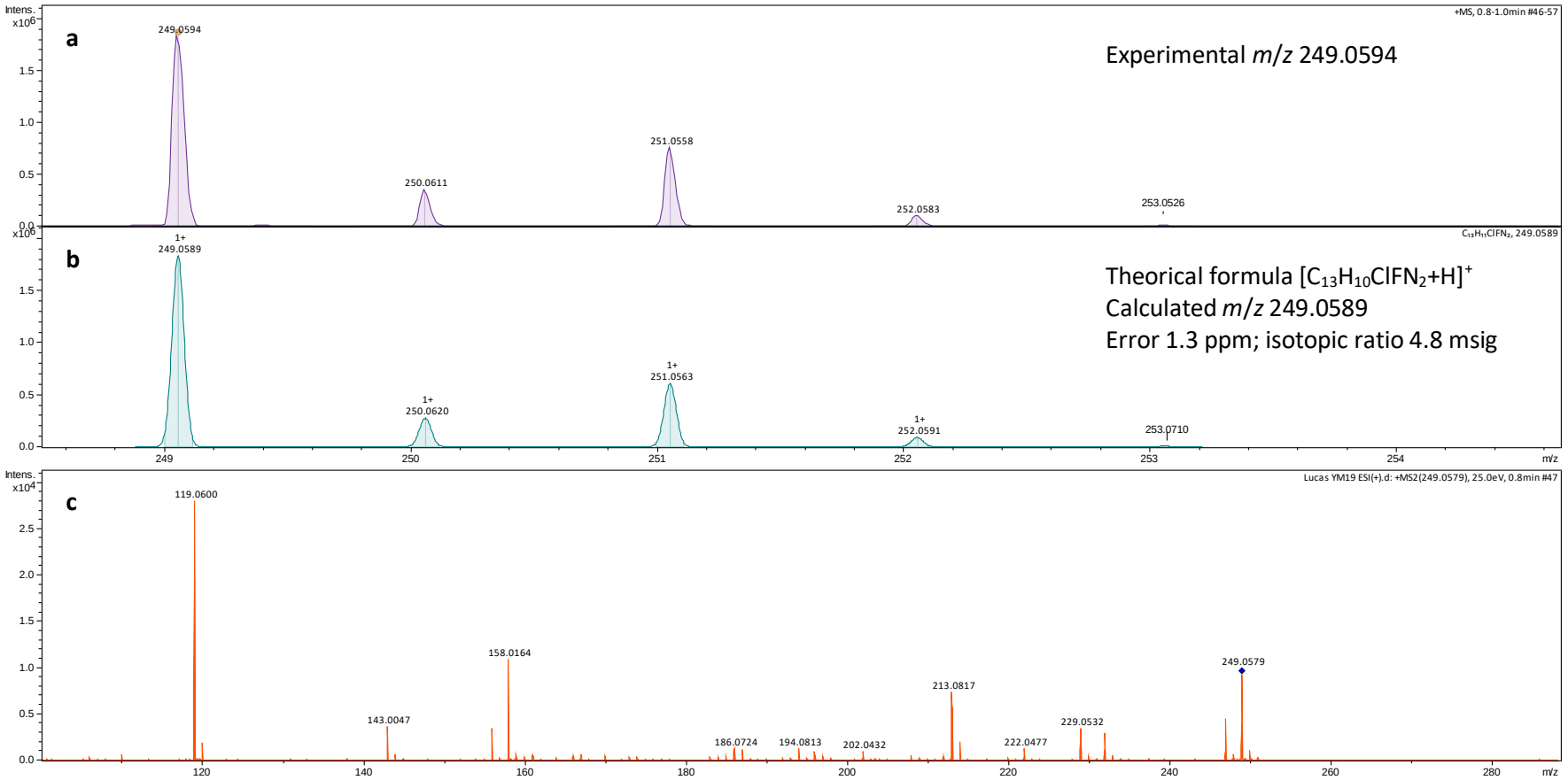


Figure S55. The HRMS analysis of compound **1i**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 248.5 and 254.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

HRMS spectra of *N*-phenyl-1*H*-indazoles

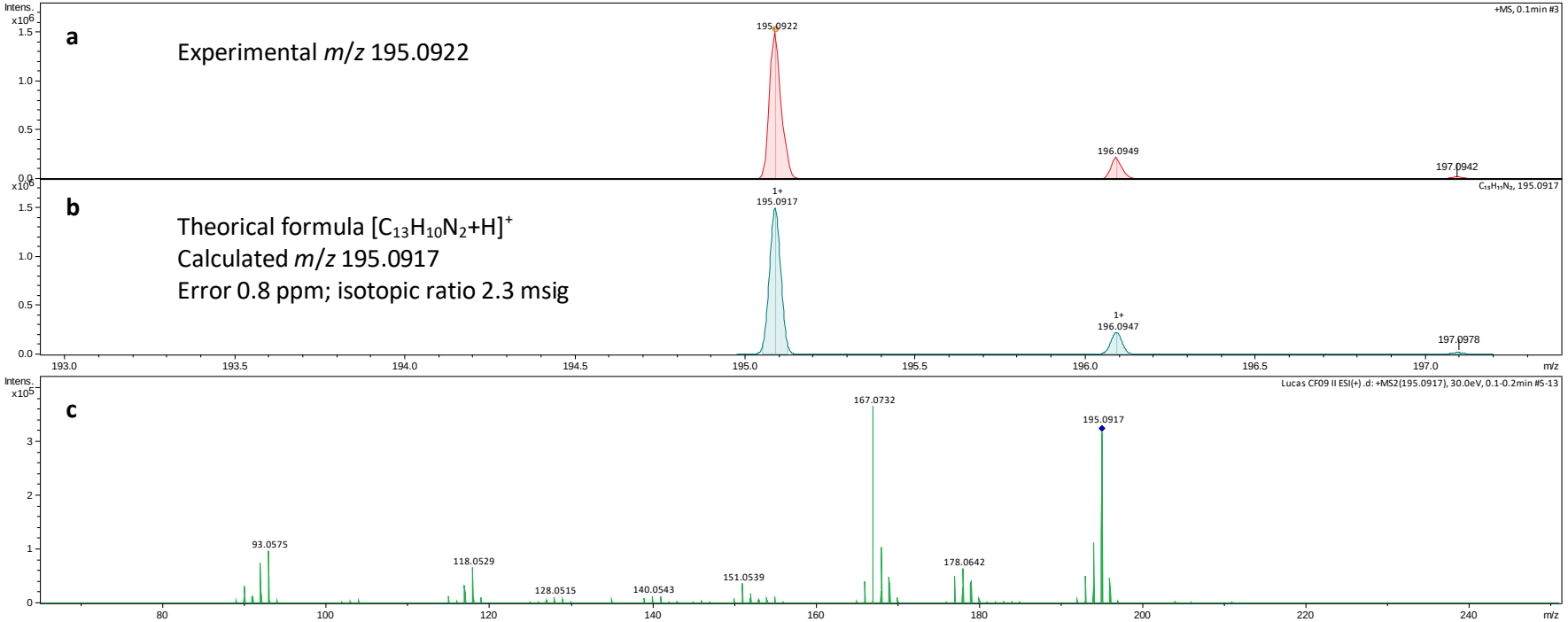


Figure S56. The HRMS analysis of compound **2a**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 192.9 and 197.4 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

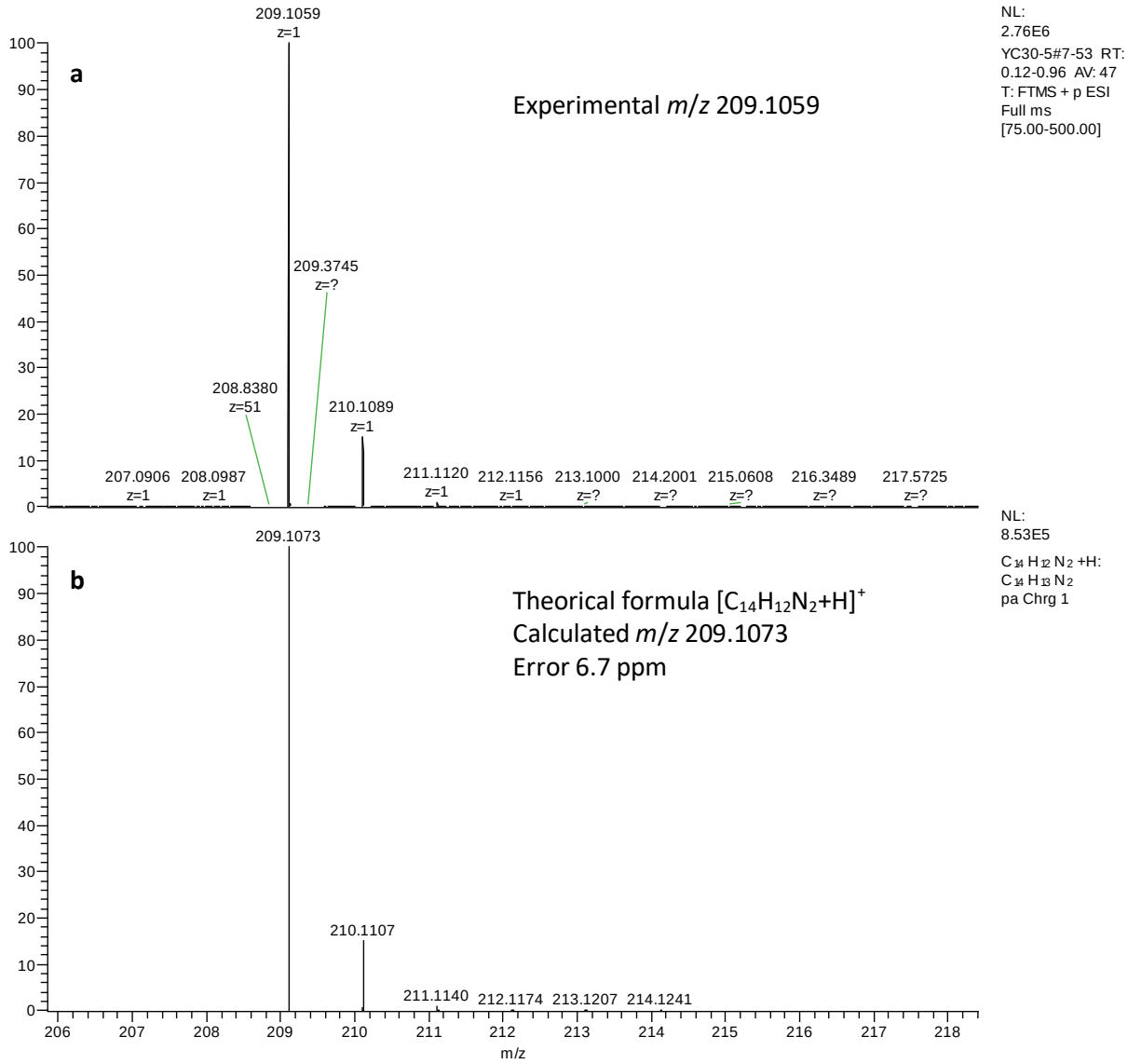


Figure S57. The HRMS analysis of compound **2b**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 205.9 and 218.4 Da highlighting the exact mass and isotopic ratio.

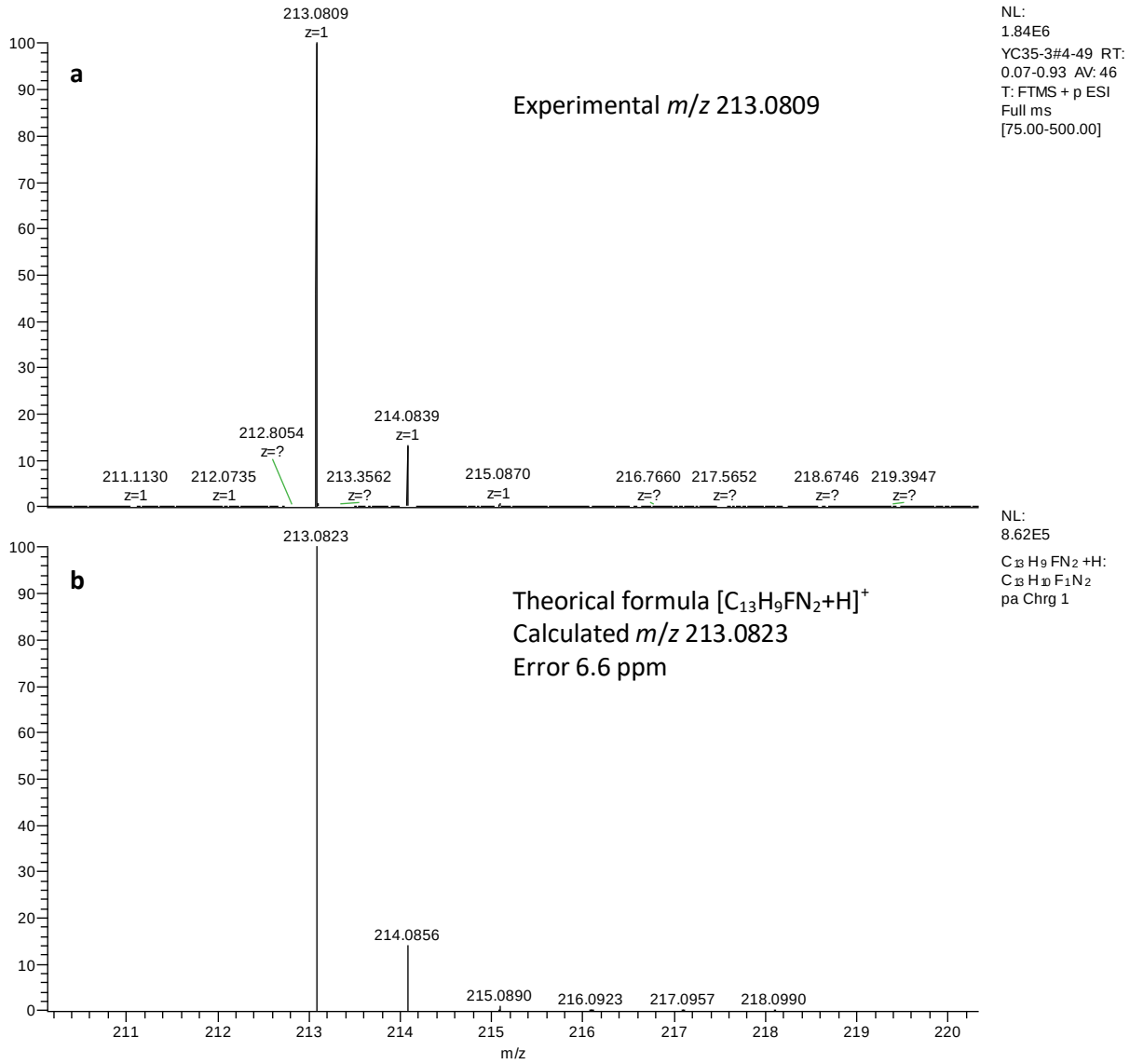


Figure S58. The HRMS analysis of compound **2d**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 210.1 and 220.3 Da highlighting the exact mass and isotopic ratio.

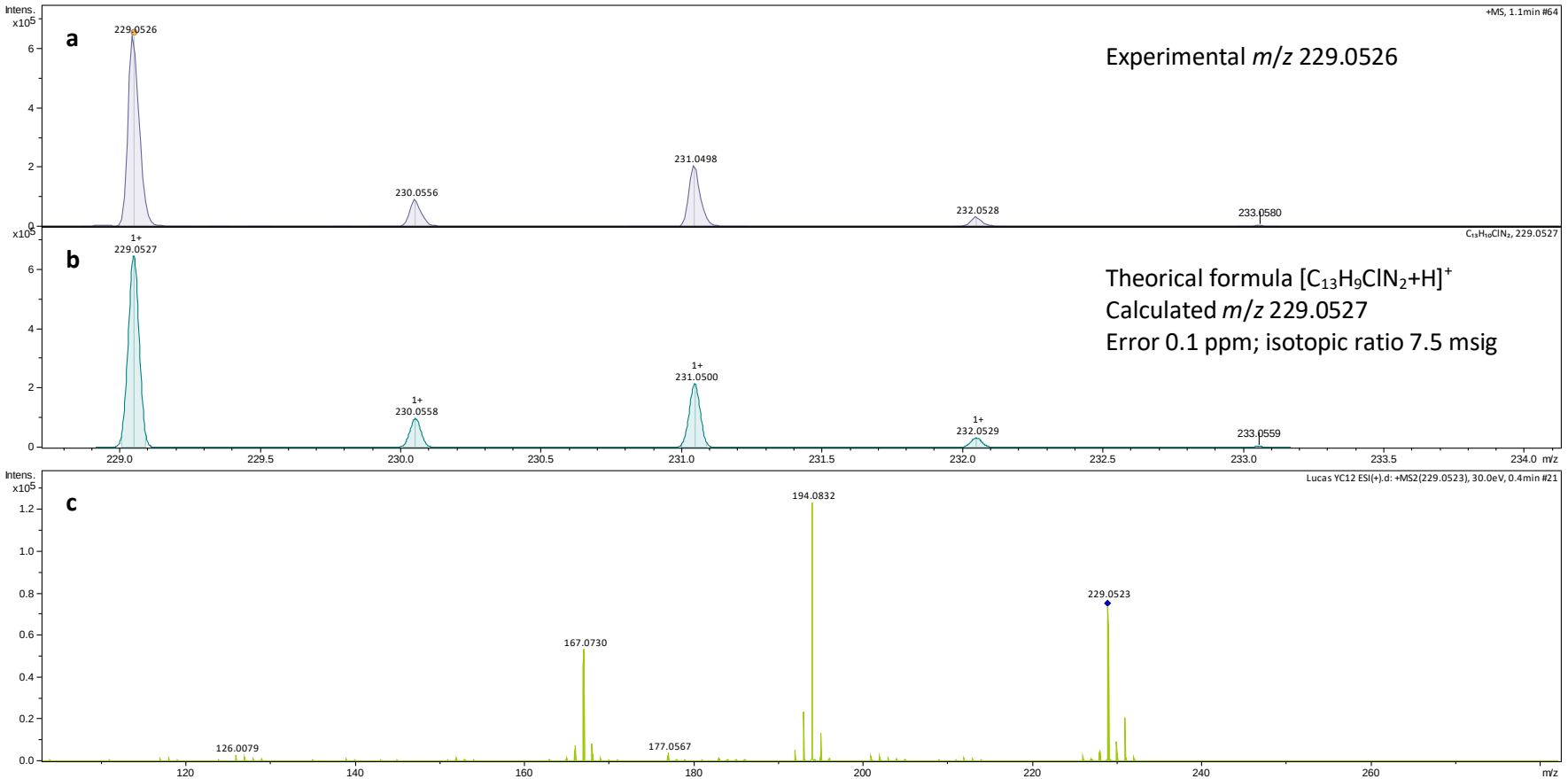


Figure S59. The HRMS analysis of compound **2e**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 228.7 and 234.1 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

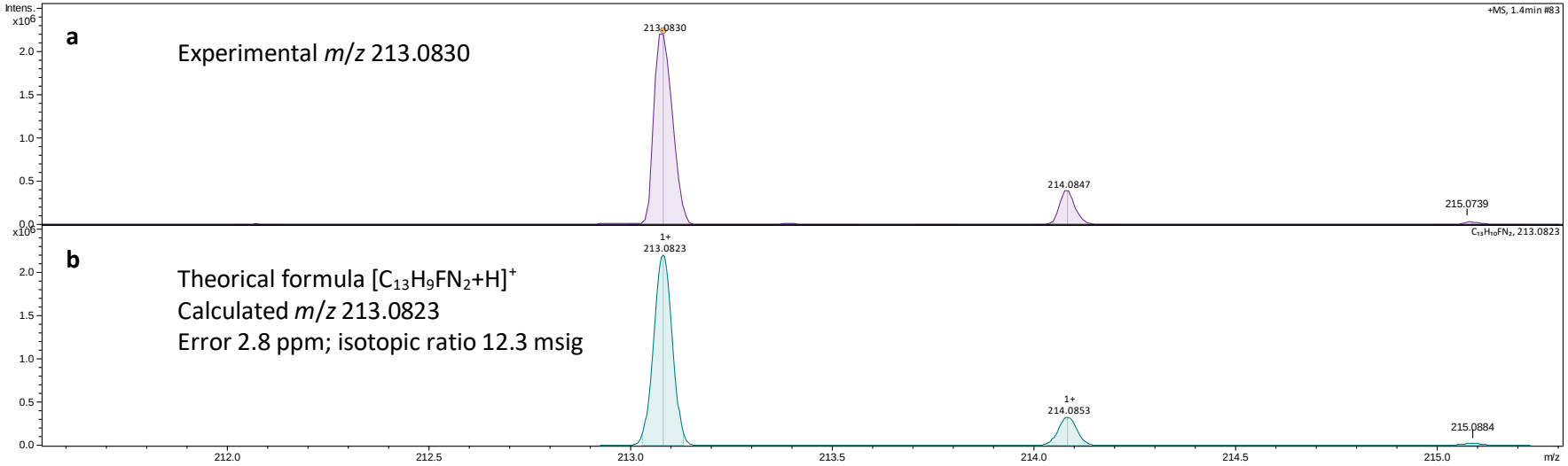


Figure S60. The HRMS analysis of compound **2f**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 211.1 and 215.6 Da highlighting the exact mass and isotopic ratio.

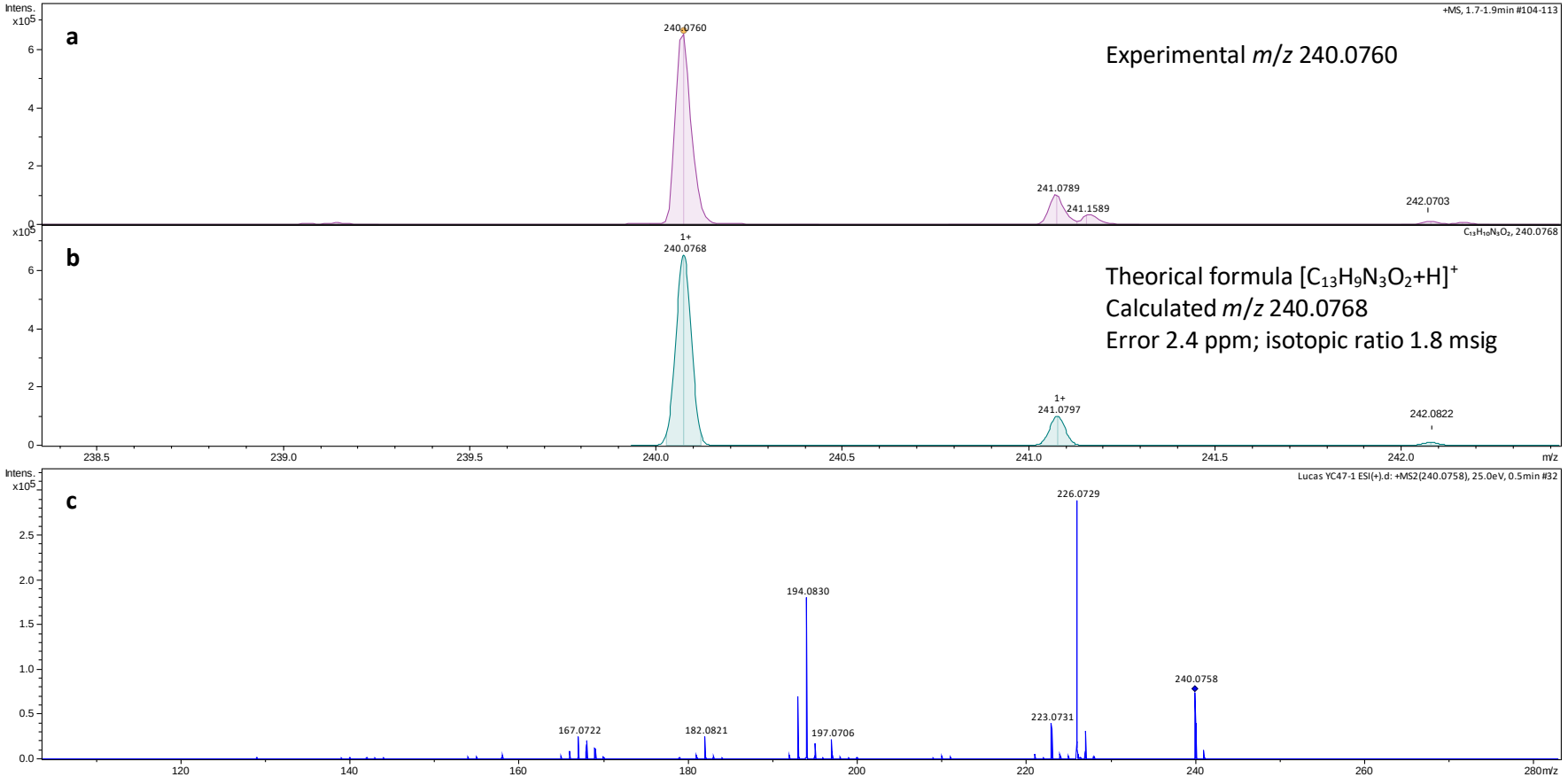


Figure S61. The HRMS analysis of compound **2g**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 238.4 and 242.4 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

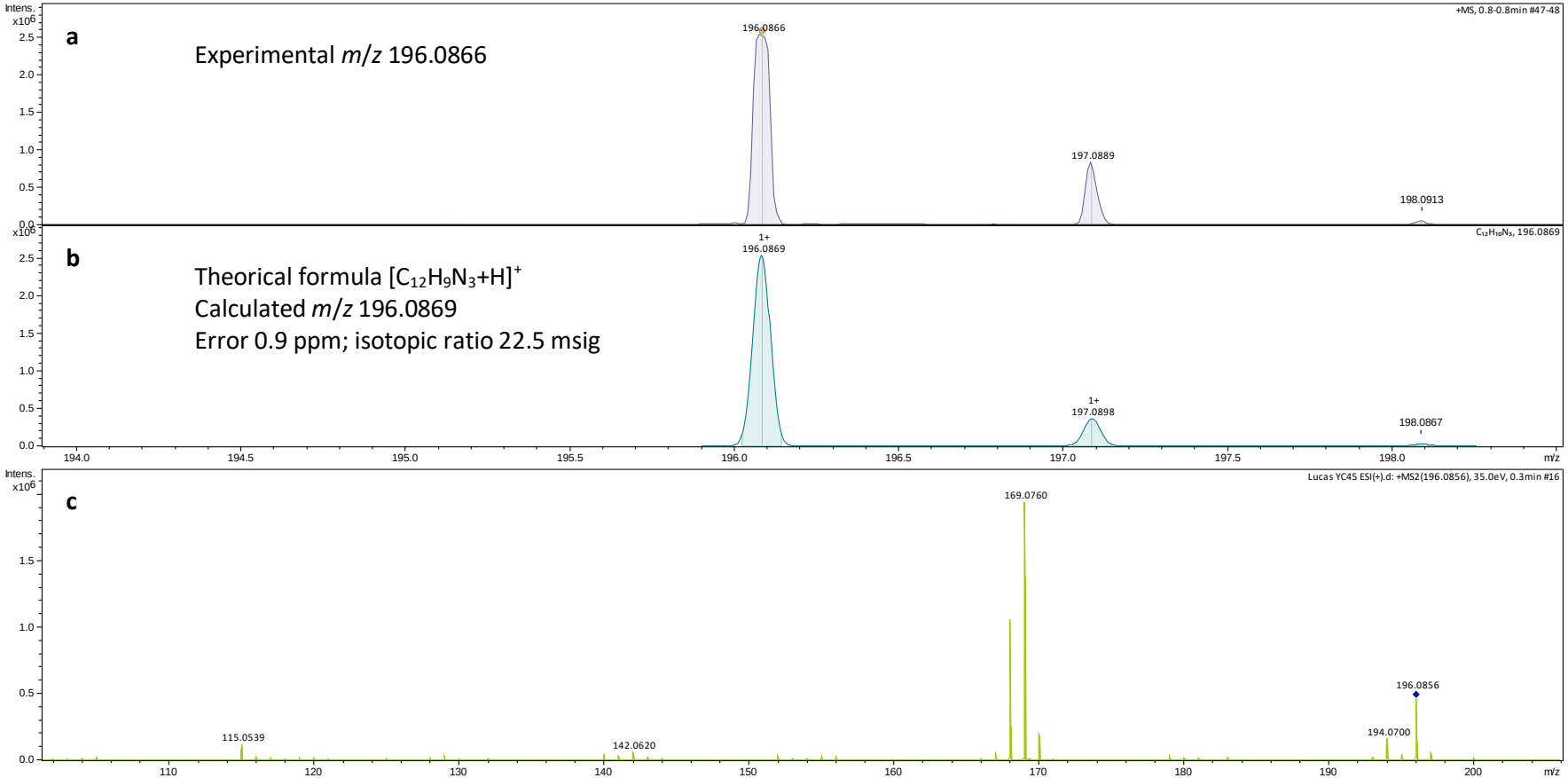


Figure S62. The HRMS analysis of compound **2h**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 193.9 and 198.5 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

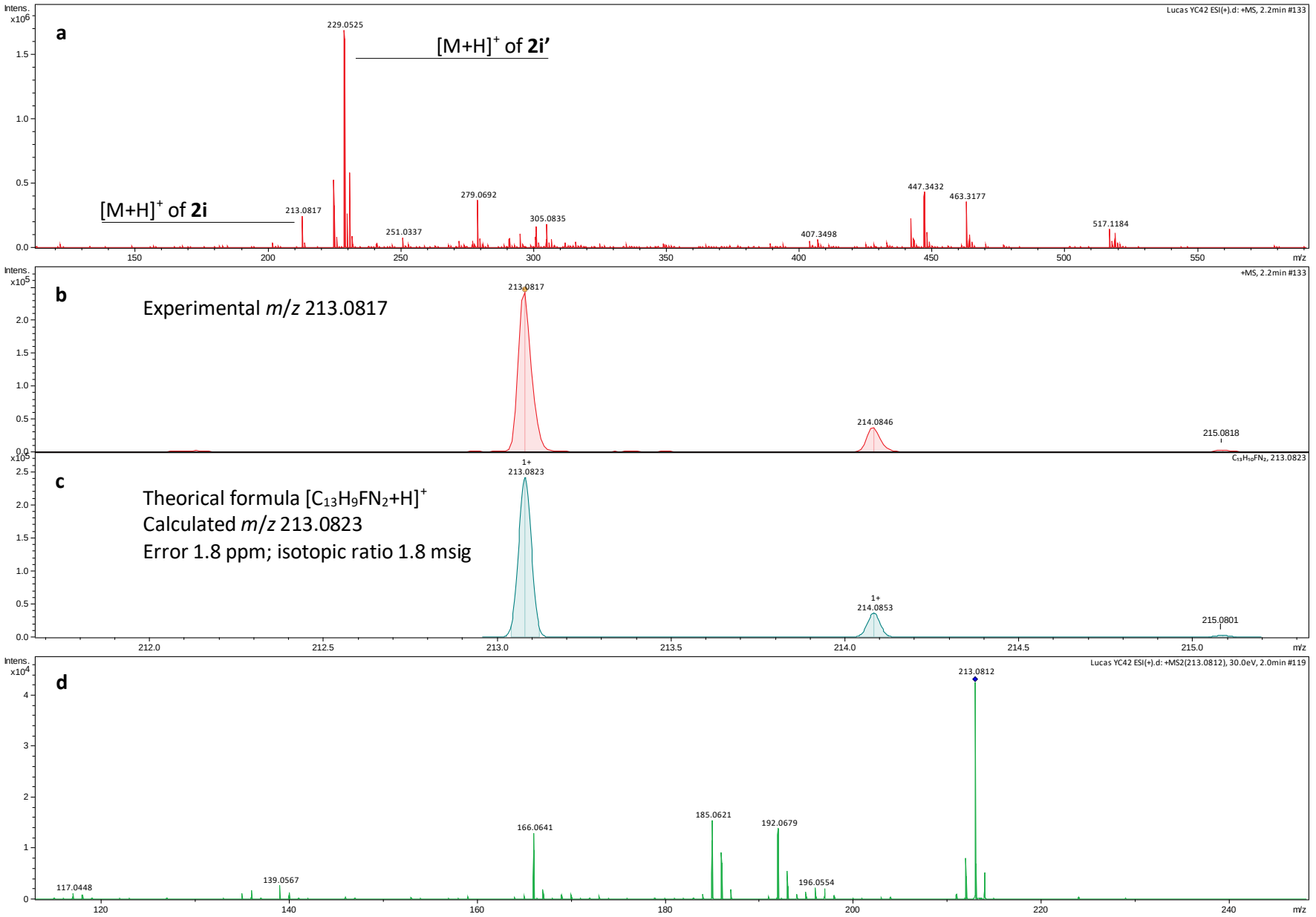


Figure S63. The HRMS analysis of the mixture of compounds **2i+2i'**. The full experimental spectrum (**a**); the experimental spectrum (**b**) and the simulated spectrum (**c**), both expanded between 211.4 and 215.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**d**) (fragmentation pathway).

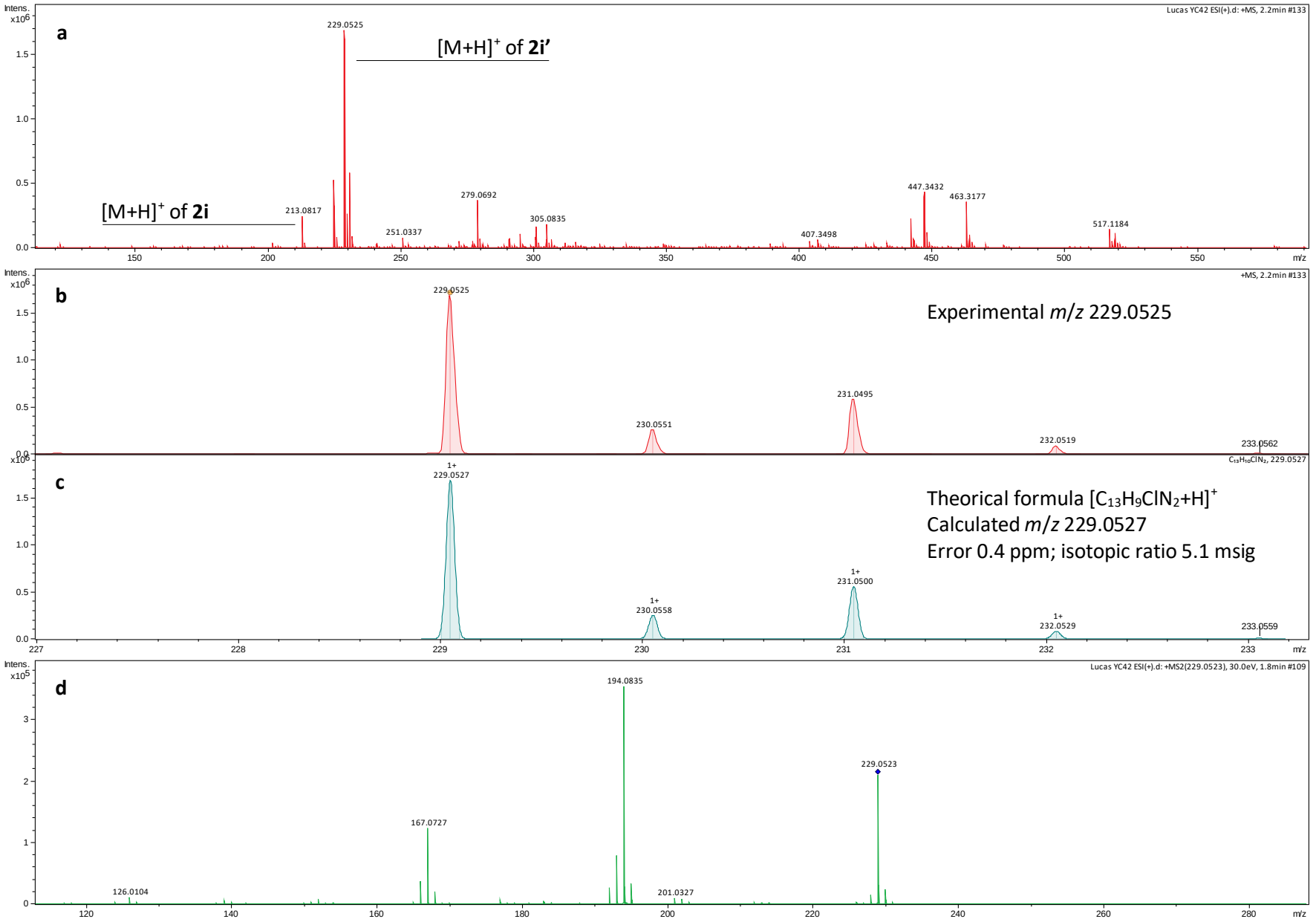


Figure S64. The HRMS analysis of the mixture of compounds **2i** and **2i'**. The full experimental spectrum (**a**); the experimental spectrum (**b**) and the simulated spectrum (**c**), both expanded between 227.0 and 233.3 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**d**) (fragmentation pathway).

HRMS spectra of *N*-thiazolylhydrazones 3a–i

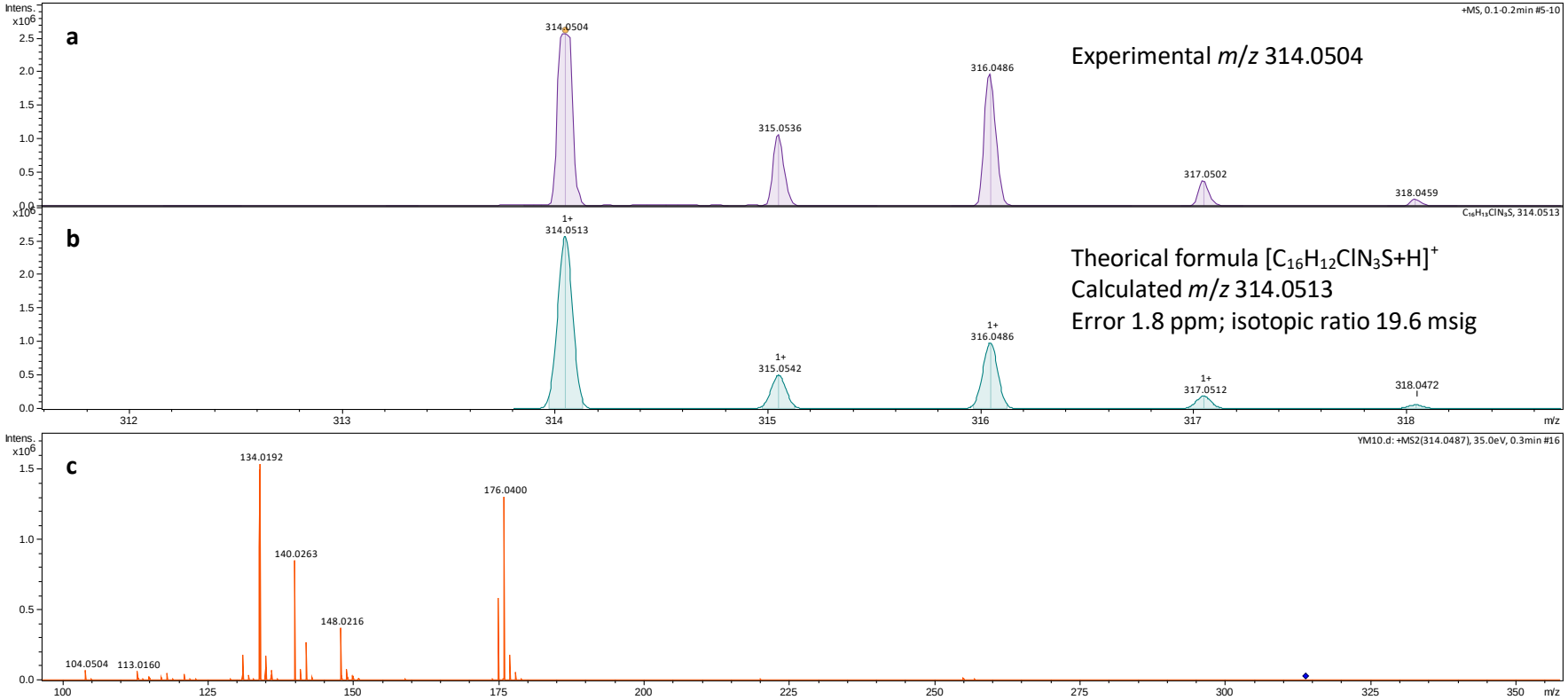


Figure S65. The HRMS analysis of compound **3a**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 311.8 and 318.7 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

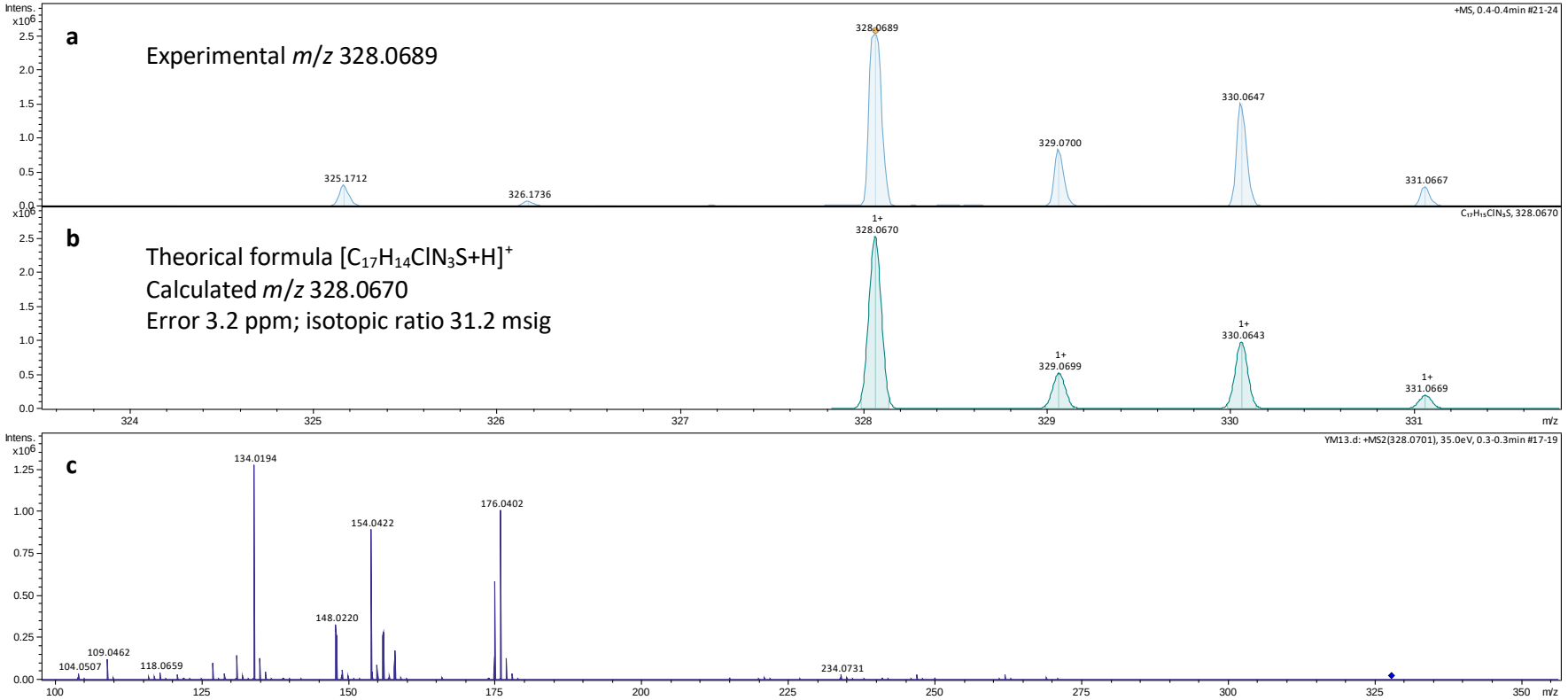


Figure S66. The HRMS analysis of compound **3b**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 323.5 and 331.8 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

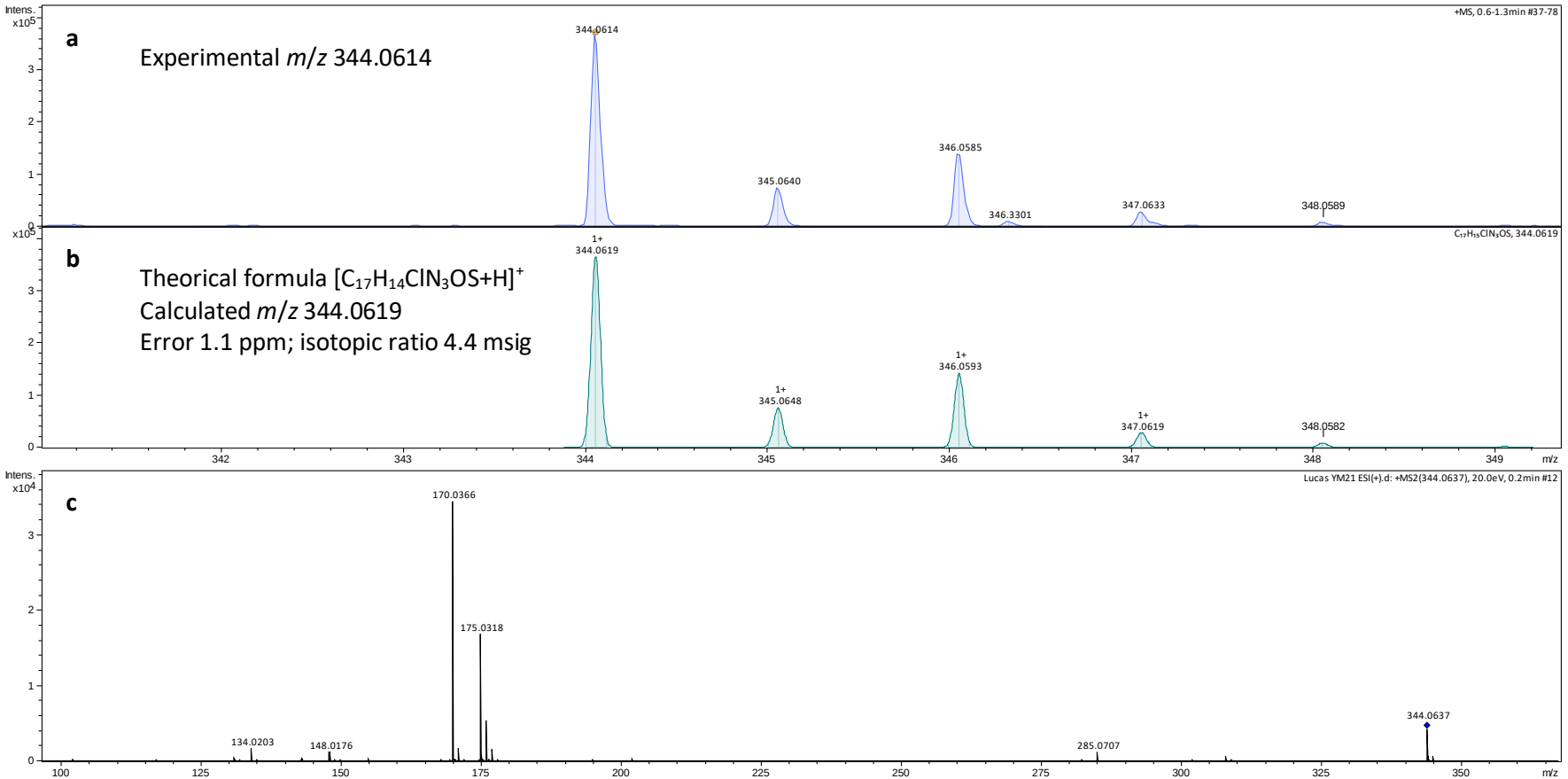


Figure S67. The HRMS analysis of compound **3c**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 341.0 and 349.2 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

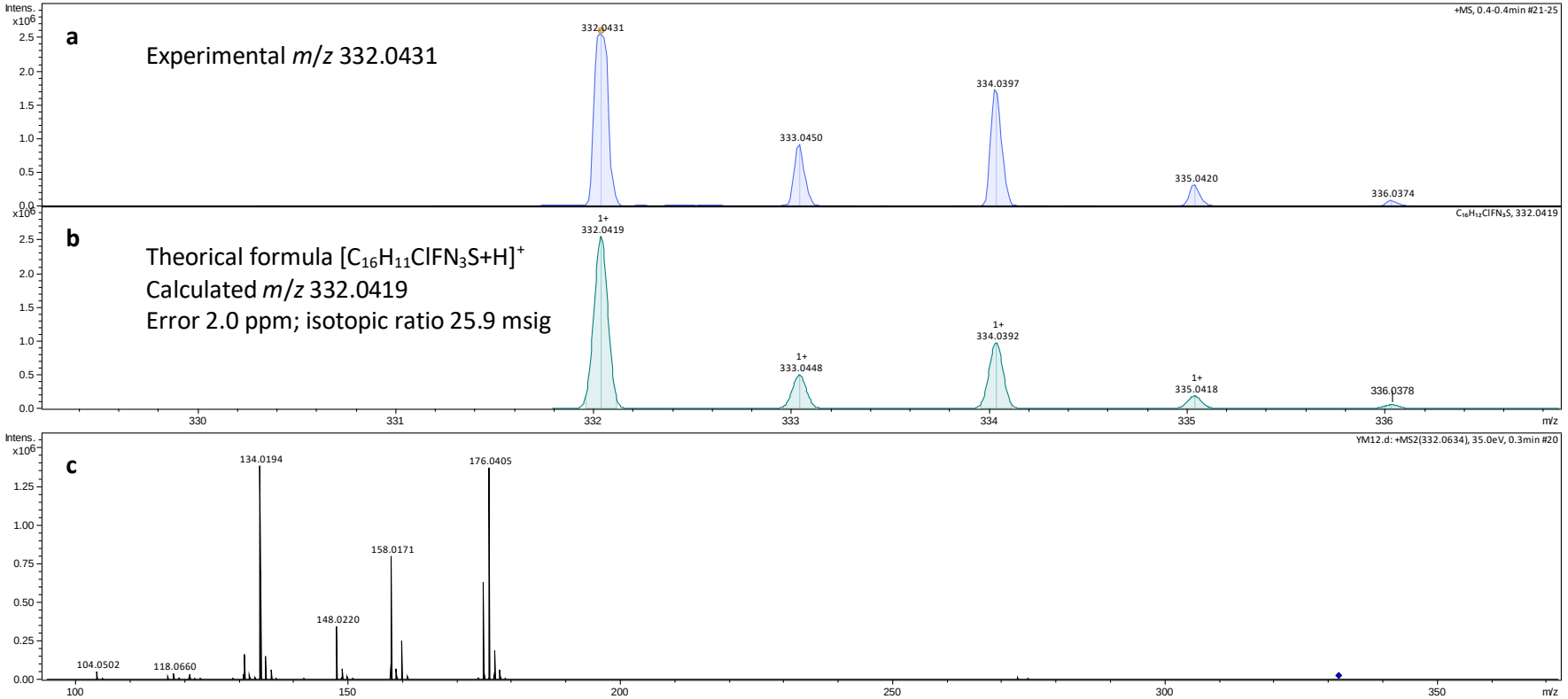


Figure S68. The HRMS analysis of compound **3d**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 329.2 and 336.9 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

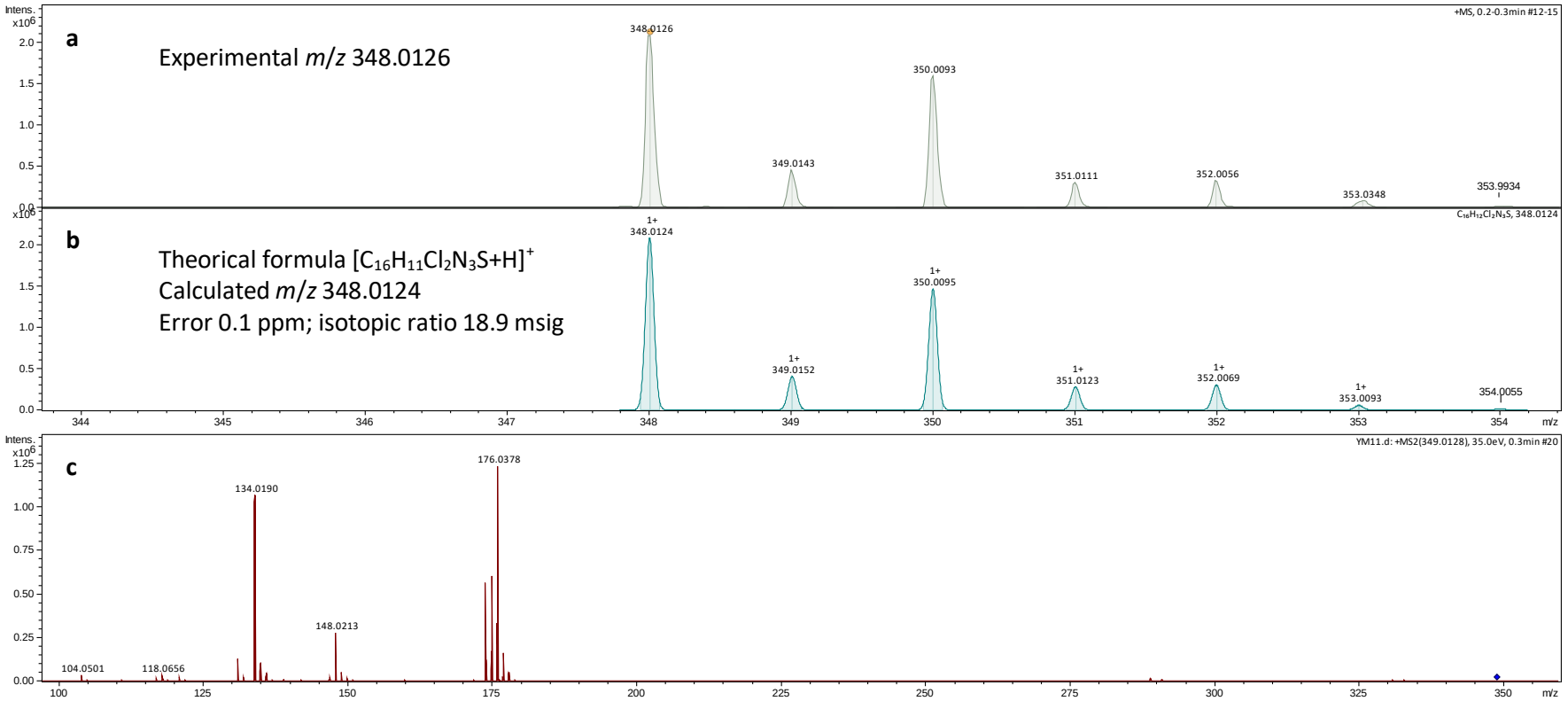


Figure S69. The HRMS analysis of compound **3e**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 343.7 and 354.4 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

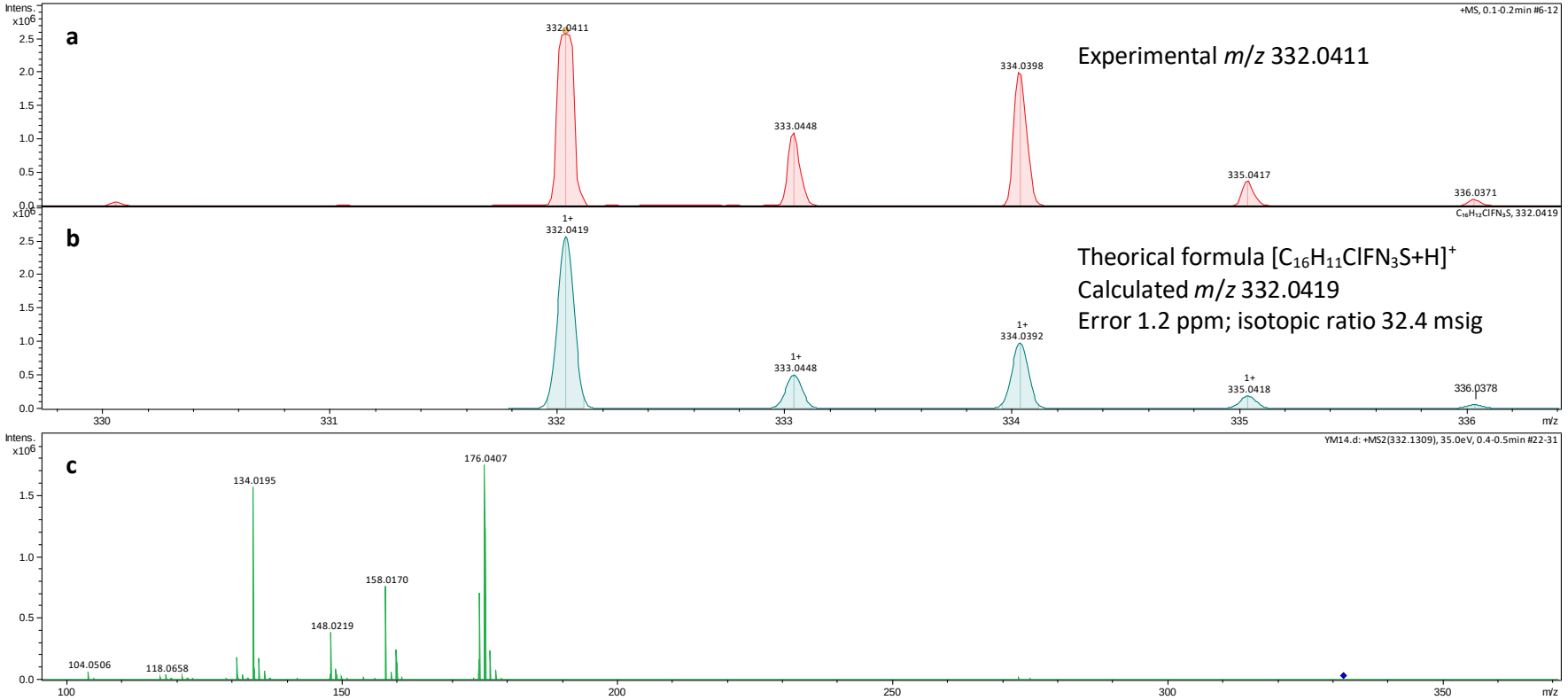


Figure S70. The HRMS analysis of compound **3f**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 329.2 and 336.9 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

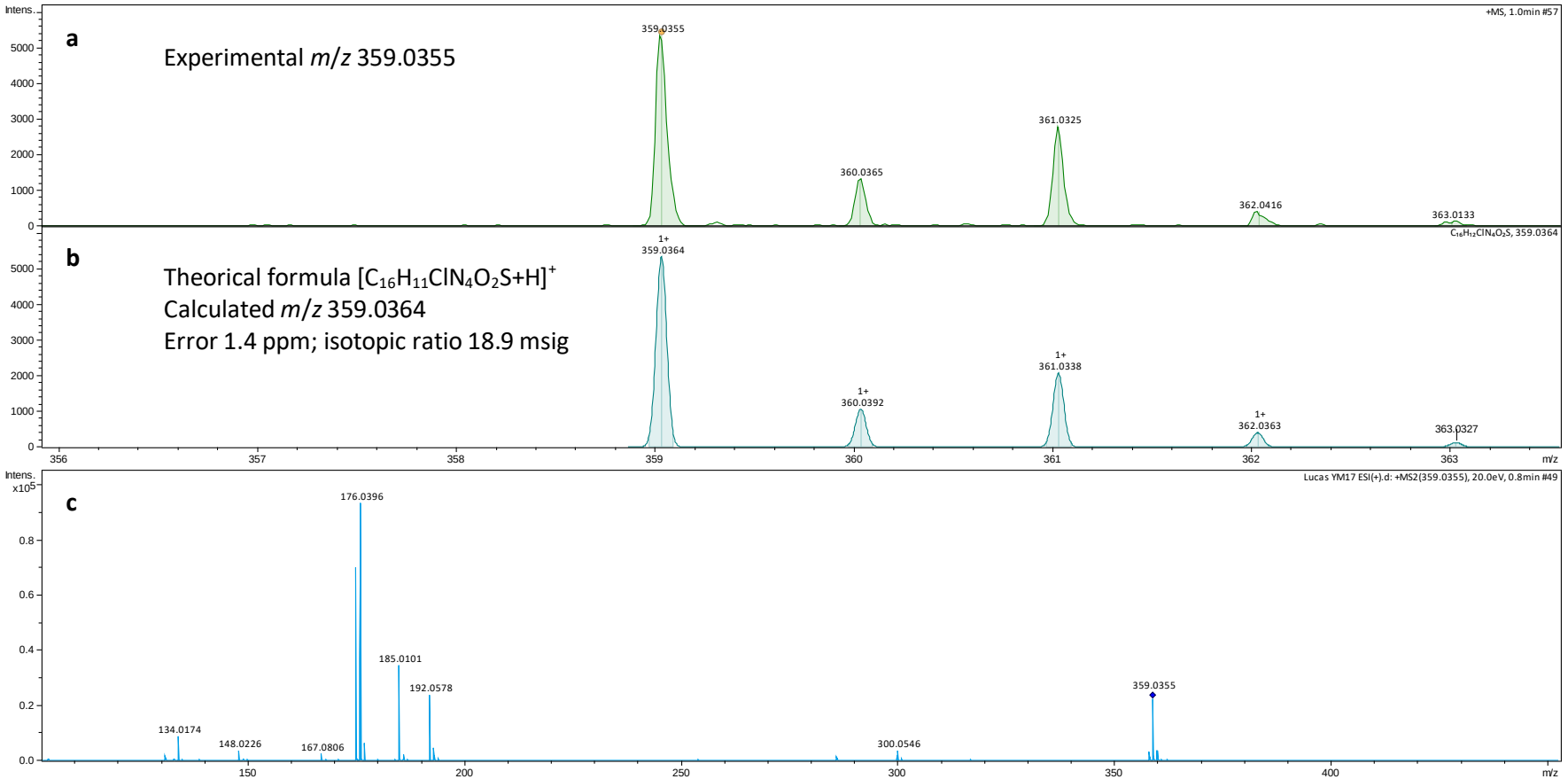


Figure S71. The HRMS analysis of compound **3g**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 356.0 and 363.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

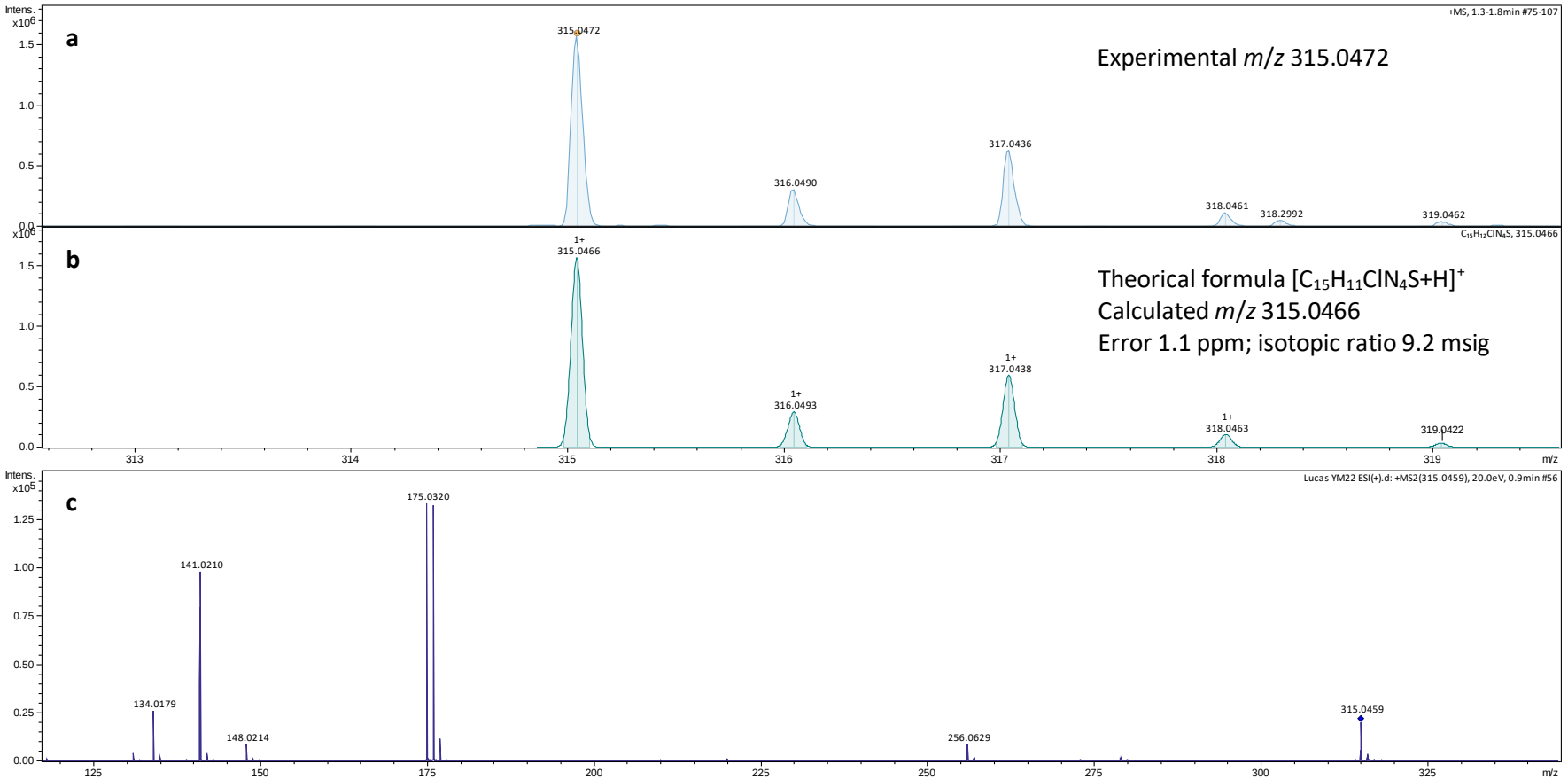


Figure S72. The HRMS analysis of compound **3h**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 312.6 and 319.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

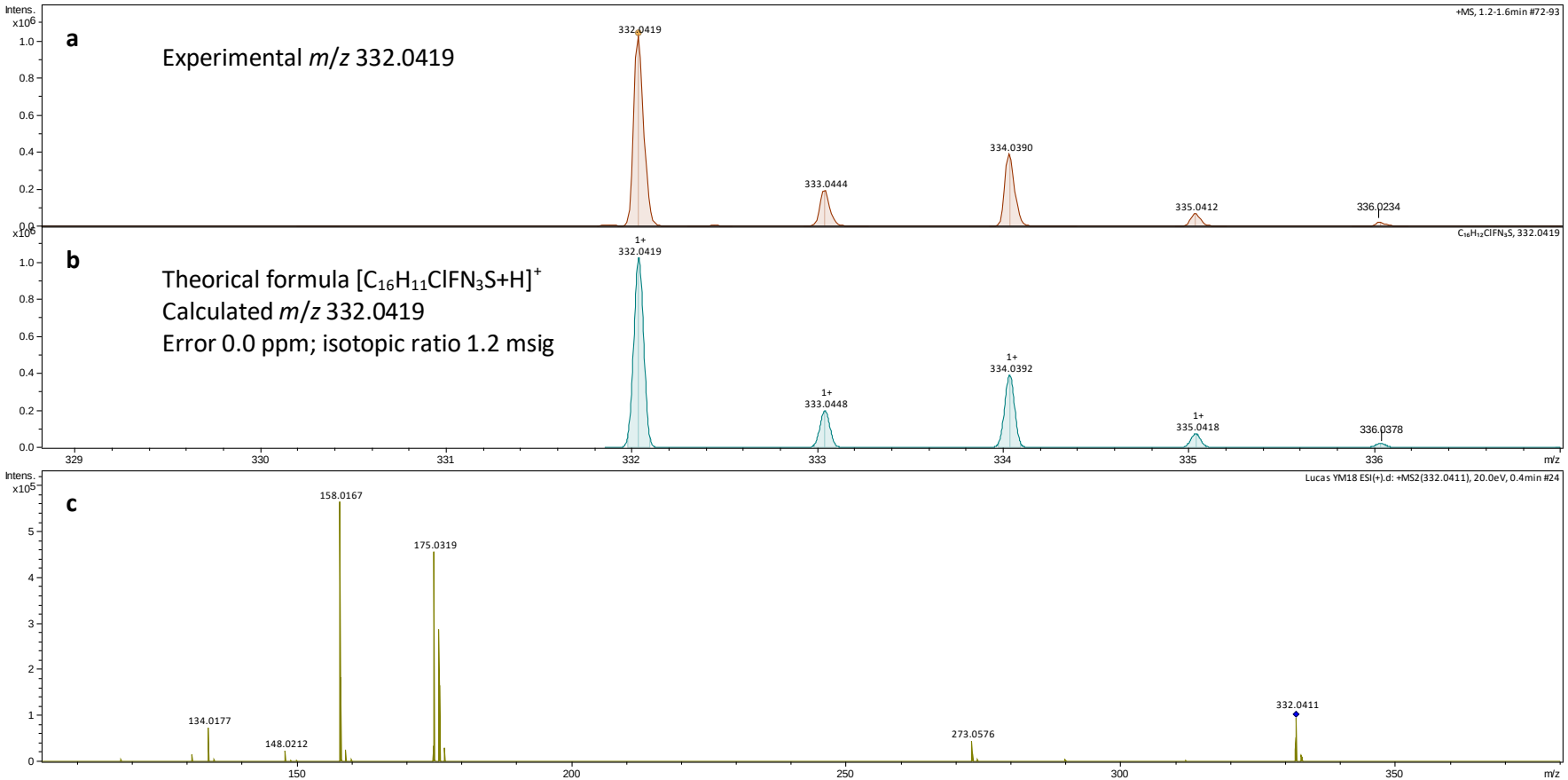


Figure S73. The HRMS analysis of compound **3i**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 328.8 and 337.0 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

HRMS spectra of *N*-thiazolyl-1*H*-indazoles

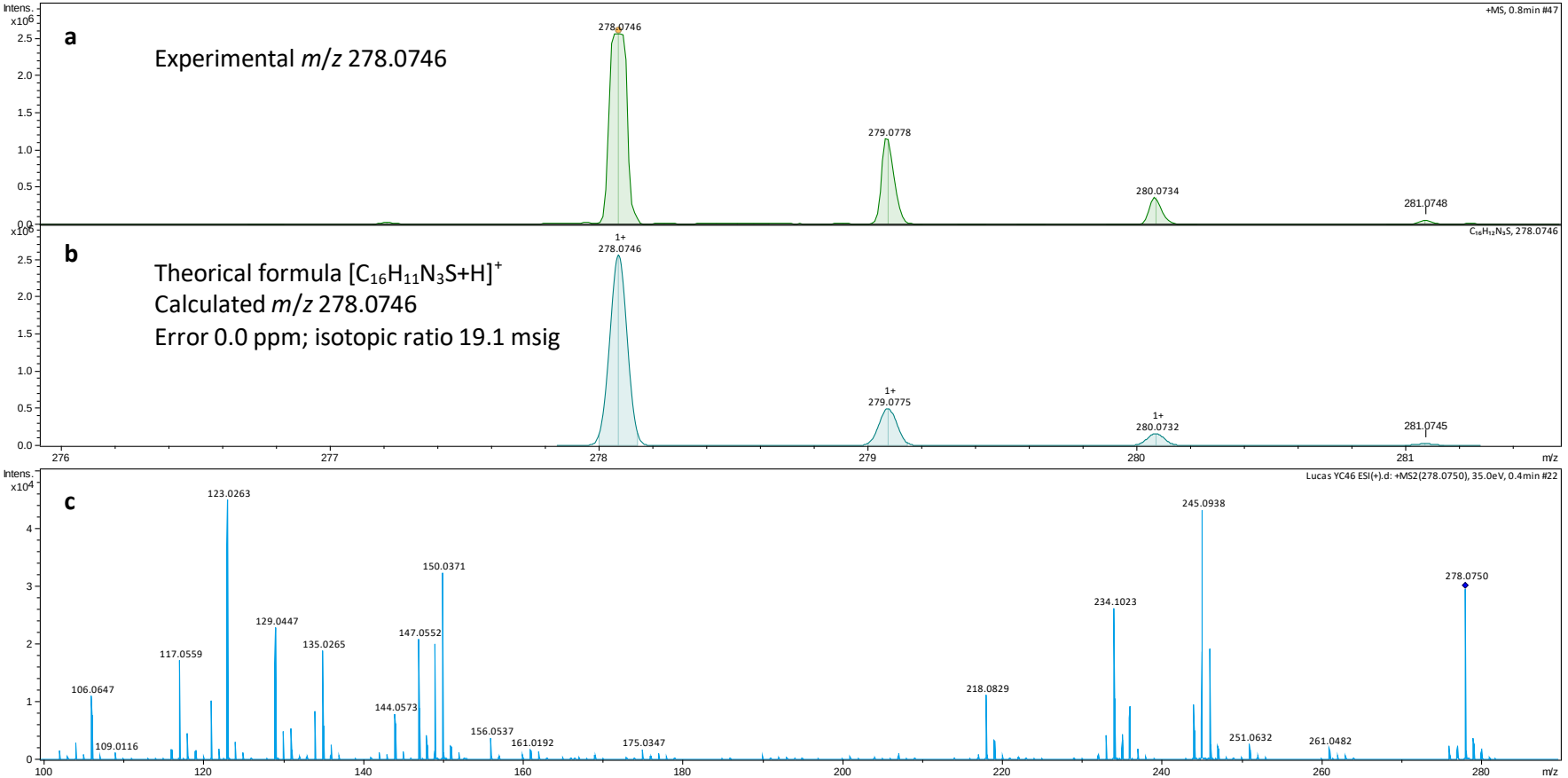


Figure S74. The HRMS analysis of compound **4a**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 275.9 and 281.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

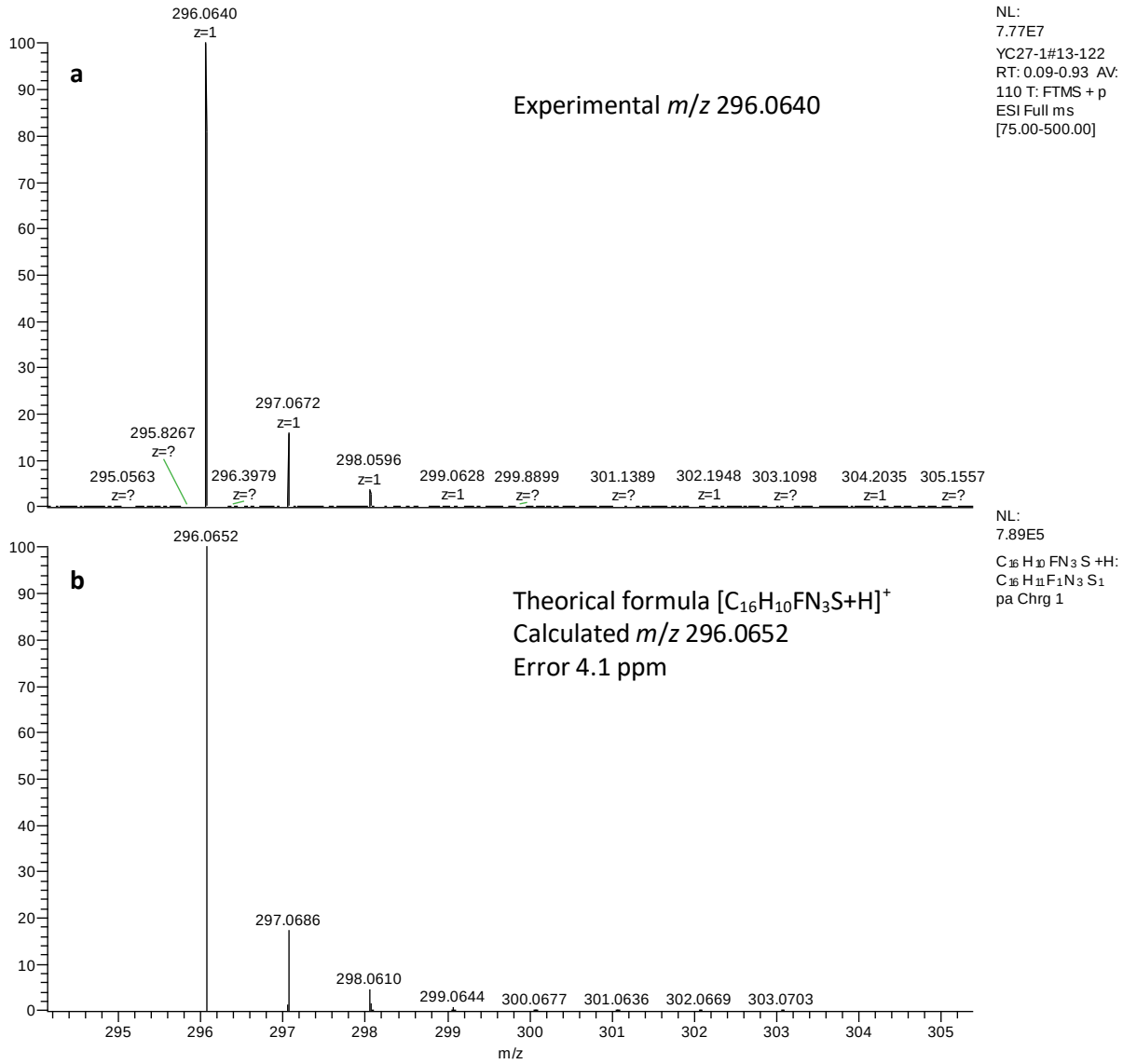


Figure S75. The HRMS analysis of compound **4d**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 294.2 and 305.4 Da highlighting the exact mass and isotopic ratio.

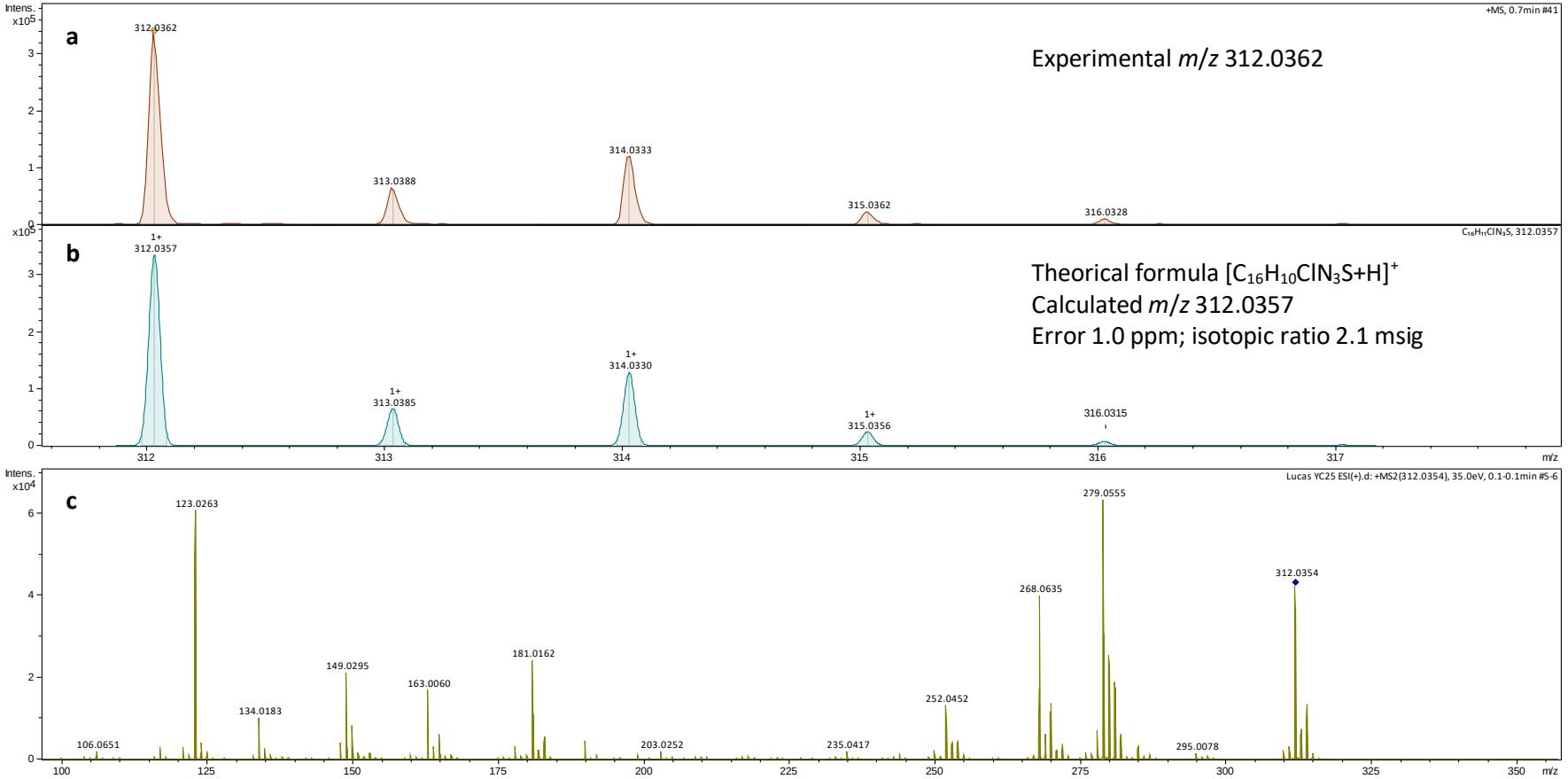


Figure S76. The HRMS analysis of compound **4e**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 311.8 and 317.9 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

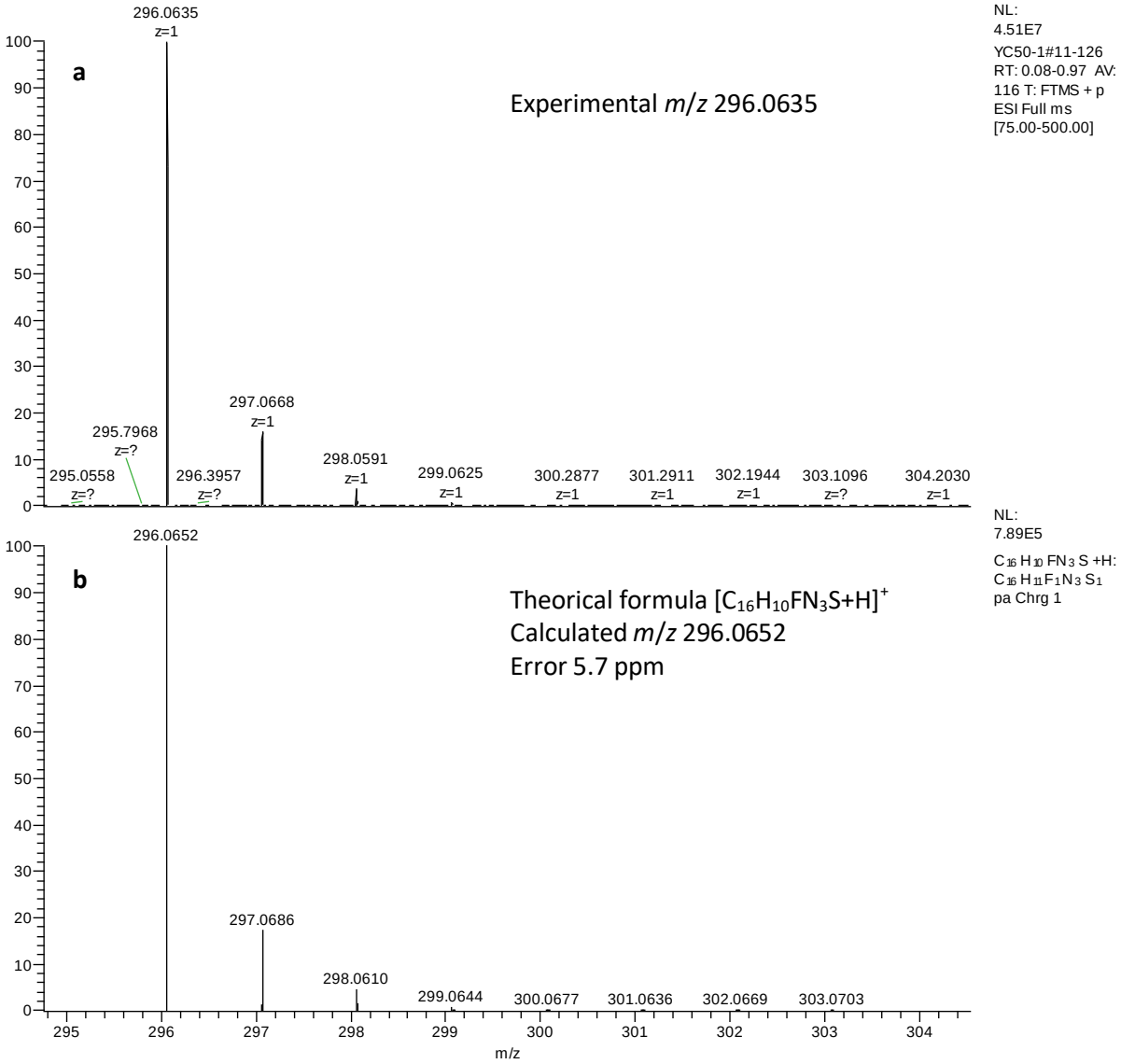


Figure S77. The HRMS analysis of compound **4f**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 294.8 and 304.5 Da highlighting the exact mass and isotopic ratio.

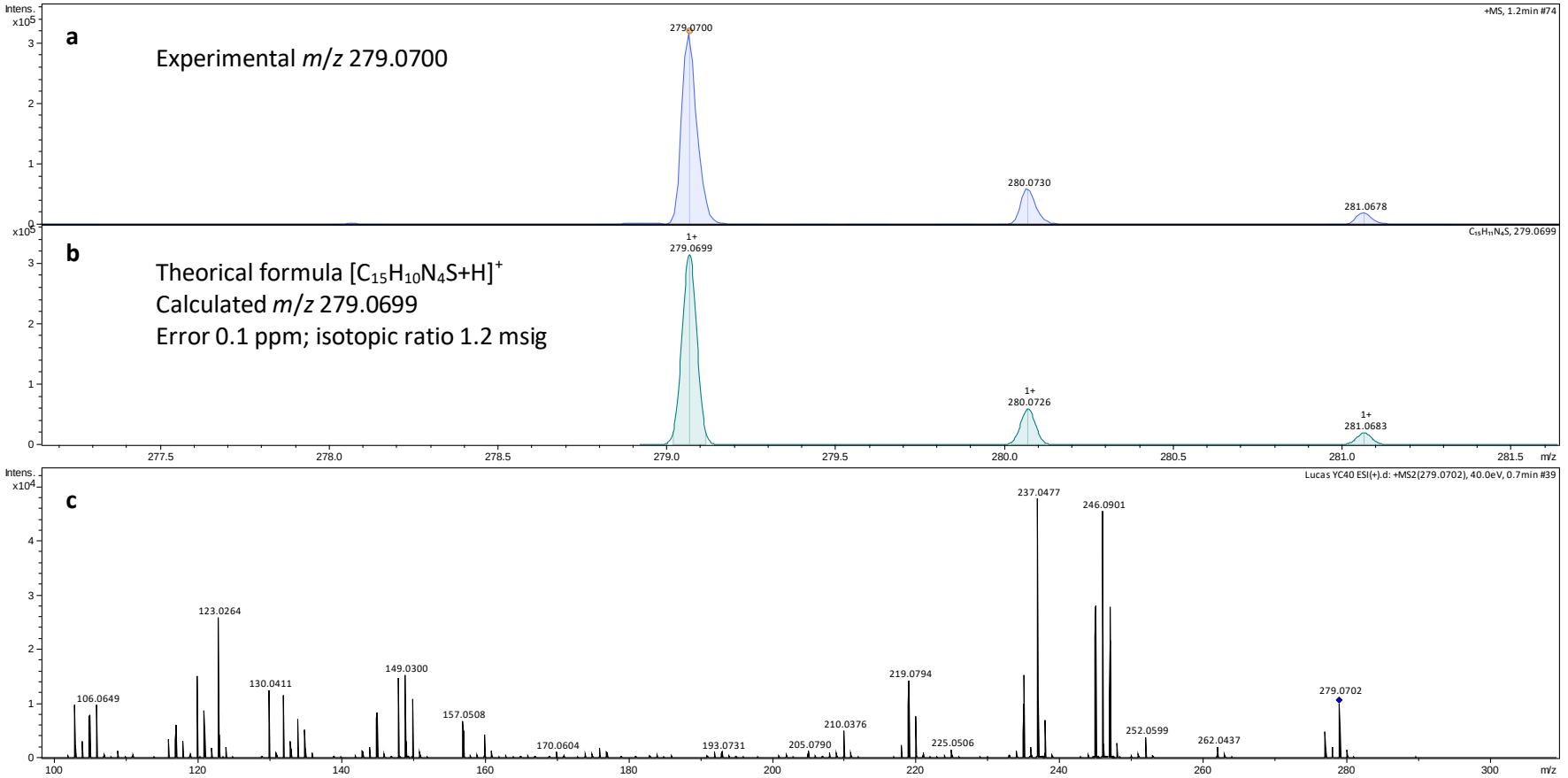


Figure S78. The HRMS analysis of compound **4h**. The experimental spectrum (**a**) and the simulated spectrum (**b**), both expanded between 275.9 and 281.6 Da highlighting the exact mass and isotopic ratio; the analysis in MS–MS mode (**c**) (fragmentation pathway).

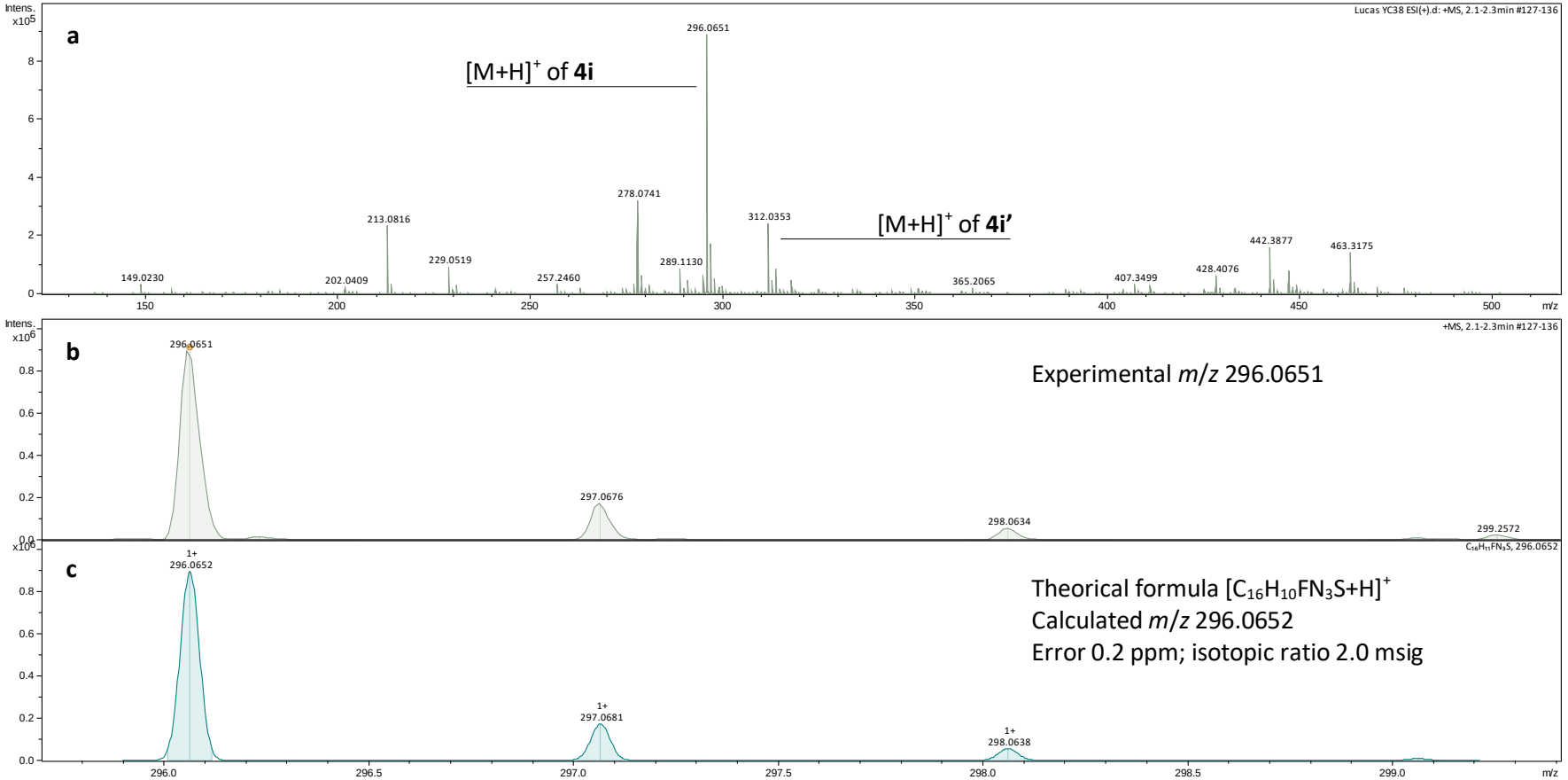


Figure S79. The HRMS analysis of the mixture of compounds **4i** and **4i'**. The full experimental spectrum (**a**); the experimental spectrum (**b**) and the simulated spectrum (**c**), both expanded between 295.6 and 299.8 Da highlighting the exact mass and isotopic ratio.

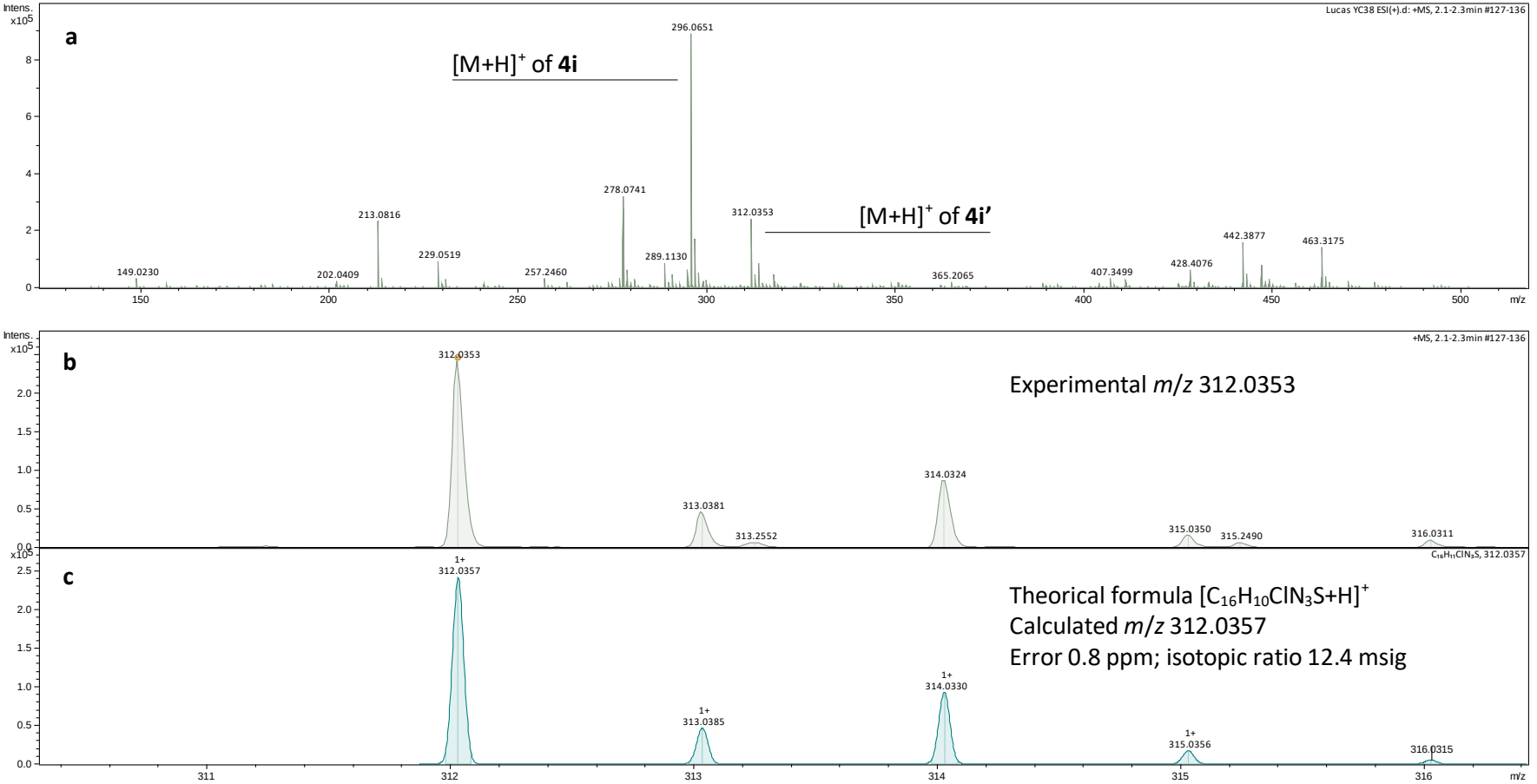


Figure S80. The HRMS analysis of the mixture of compounds **4i** and **4i'**. The full experimental spectrum (**a**); the experimental spectrum (**b**) and the simulated spectrum (**c**), both expanded between 310.3 and 316.4 Da highlighting the exact mass and isotopic ratio.

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