

# Reaction of *N'*-(2-alkynylbenzylidene)hydrazide with tertiary amine: A concise synthesis of *H*-pyrazolo[5,1-*a*]isoquinolines

Chao Ye,<sup>a</sup> Xingxin Yu,<sup>a</sup> Guanyinsheng Qiu,<sup>a</sup> and Jie Wu<sup>\*a,b</sup>

<sup>a</sup> Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China

<sup>b</sup> State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,  
Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

jie\_wu@fudan.edu.cn

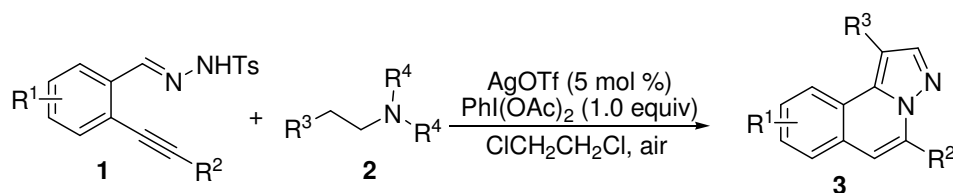
## Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S10).
3. <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **3** (S11-S52).

### General experimental methods:

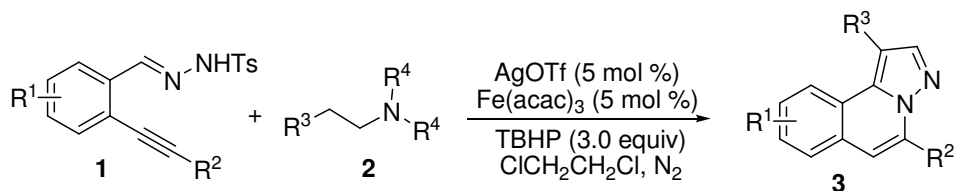
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35 °C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the synthesis of H-pyrazolo[5,1-a]isoquinolines via a reaction of N'-(2-alkynylbenzylidene)hydrazide 1 with tertiary amine 2*

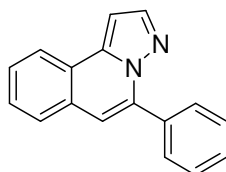


A mixture of *N'*-(2-alkynylbenzylidene)hydrazides **1** (0.30 mmol), AgOTf (5 mol %) in DCE (1.0 mL) was stirred at 60 °C in air for 30 min. Then the reaction was cooled to 30 °C, PhI(OAc)<sub>2</sub> (0.30 mmol, 1.0 equiv) and tertiary amine **2** (1.5 mmol, 5.0 equiv) in DCE (1.0 mL) were added. The mixture was stirred under the condition indicated in Table 2. After completion of reaction as indicated by TLC, water (10 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layers was washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (eluted with PE/EA = 30:1) on

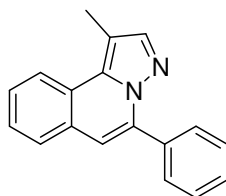
provide product **3**.



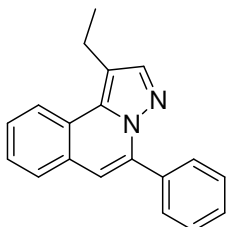
A mixture of *N*'-(2-alkynylbenzylidene)hydrazides **1** (0.30 mmol),  $\text{AgOTf}$  (5 mol %) in DCE (1.0 mL) was stirred at 60 °C in air for 30 min. Then the reaction was cooled to 30 °C,  $\text{Fe}(\text{acac})_3$  (5 mol %) and tertiary amine **2** (1.5 mmol, 5.0 equiv) in DCE (1.0 mL) were added under  $\text{N}_2$ . Then TBHP (0.9 mmol, 3.0 equiv) was added dropwise slowly at room temperature. After completion of the reaction as indicated by TLC, water (10 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layers was washed with brine (15 mL), dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (eluted with PE/EA = 30:1) to provide product **3**.



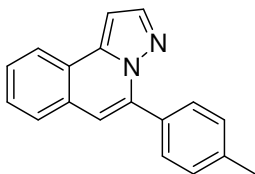
5-PhenylH-pyrazolo[5,1-*a*]isoquinoline **3a**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.03 (s, 1H), 7.07 (d,  $J = 2.2$  Hz, 1H), 7.49-7.55 (m, 5H), 7.72 (dd,  $J = 8.0, 2.2$  Hz, 1H), 7.86-7.89 (m, 2H), 7.99 (d,  $J = 2.5$  Hz, 1H), 8.10 (dd,  $J = 8.0, 2.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  97.8, 112.5, 123.4, 124.0, 127.0, 127.3, 127.9, 128.3, 129.1, 129.2, 129.3, 133.8, 138.4, 139.2, 140.8; HRMS calcd. for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 267.0893, found 268.0897.



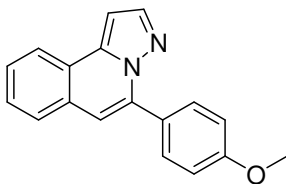
1-Methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3b**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.64 (s, 3H), 6.95 (s, 1H), 7.47-7.53 (m, 5H), 7.70 (d,  $J = 8.2$  Hz, 1H), 7.80 (s, 1H), 7.83-7.85 (m, 2H), 8.26 (d,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.8, 110.0, 112.2, 123.1, 125.6, 127.0, 128.3, 129.1, 129.3, 129.4, 134.0, 135.1, 138.5, 141.9; HRMS calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 281.1049, found 281.1039.



1-Ethyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3c**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.45 (t,  $J = 7.5$  Hz, 3H), 3.09 (q,  $J = 7.5$  Hz, 2H), 6.96 (s, 1H), 7.48- 7.55 (m, 5H), 7.70 (d,  $J = 7.1$  Hz, 1H), 8.24 (d,  $J = 8.2$  Hz, 1H), 8.82-8.85 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 19.4, 112.3, 117.0, 123.1, 125.4, 127.0, 127.1, 127.2, 128.3, 129.1, 129.3, 129.4, 134.0, 134.4, 138.5, 140.2; HRMS calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2^+$   $[\text{M}+\text{H}]^+$ : 273.1386, found 273.1380.

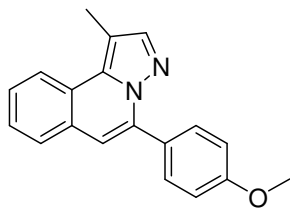


5-*p*-Tolyl*H*-pyrazolo[5,1-*a*]isoquinoline **3d**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.43 (s, 3H), 7.01 (s, 1H), 7.06 (s, 1H), 7.33 (d,  $J = 7.3$  Hz, 2H), 7.30-7.55 (m, 2H), 7.71 (d,  $J = 7.7$  Hz, 1H), 7.76 (d,  $J = 6.8$  Hz, 2H), 7.98 (s, 1H), 8.09 (d,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 97.7, 112.0, 123.4, 123.9, 127.0, 127.1, 127.8, 129.0, 129.1, 129.2, 130.8, 139.2, 140.7; HRMS calcd. for  $\text{C}_{18}\text{H}_{15}\text{N}_2^+$   $[\text{M}+\text{H}]^+$ : 259.1230, found 259.1239.

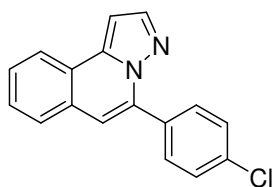


5-(4-Methoxyphenyl)*H*-pyrazolo[5,1-*a*]isoquinoline **3e**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.87 (s, 3H), 6.99 (s, 1H), 7.03-7.06 (m, 3H), 7.52 (t,  $J = 3.68$  Hz, 2H), 7.70-7.75 (m,

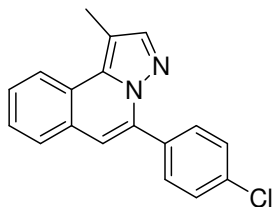
1H), 7.83 (d,  $J = 8.2$  Hz, 2H), 7.99 (s, 1H), 8.08 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  55.3, 97.7, 111.8, 113.7, 123.4, 123.7, 126.1, 126.9, 127.0, 127.8, 129.2, 130.7, 140.6, 160.2; HRMS calcd. for  $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 275.1179, found 275.1187.



5-(4-Methoxyphenyl)-1-methyl*H*-pyrazolo[5,1-*a*]isoquinoline **3f**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.65 (s, 3H), 3.87 (s, 3H), 6.93 (s, 1H), 7.04 (d,  $J = 8.2$  Hz, 2H), 7.48-7.55 (m, 2H), 7.71 (d,  $J = 7.3$  Hz, 1H), 7.80 (t,  $J = 4.1$  Hz, 3H), 8.27 (d,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.8, 55.3, 109.9, 111.6, 113.7, 123.1, 125.4, 126.3, 126.8, 126.9, 127.0, 128.1, 129.5, 130.7, 135.0, 138.3, 141.8; HRMS calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 289.1335, found 289.1337.

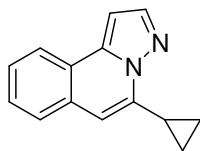


5-(4-Chlorophenyl)*H*-pyrazolo[5,1-*a*]isoquinoline **3g**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.02 (s, 1H), 7.08 (s, 1H), 7.49 (d,  $J = 7.3$  Hz, 2H), 7.54-7.59 (m, 2H), 7.72 (d,  $J = 6.8$  Hz, 1H), 7.82 (d,  $J = 7.3$  Hz, 2H), 7.98 (s, 1H), 8.11 (d,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  97.8, 123.7, 128.3, 128.7, 128.9, 129.5, 129.9, 130.0, 132.9, 137.8, 138.6, 141.4; HRMS calcd. for  $\text{C}_{17}\text{H}_{12}\text{ClN}_2^+$   $[\text{M}+\text{H}]^+$ : 279.0684, found 279.0694.

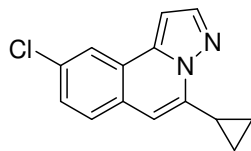


5-(4-Chlorophenyl)-1-methyl*H*-pyrazolo[5,1-*a*]isoquinoline **3h**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.64 (s, 3H), 6.93 (s, 1H), 7.46-7.59 (m, 5H), 7.71 (d,  $J = 7.3$  Hz, 1H), 7.78-7.79 (m, 3H), 8.27 (d,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.7,

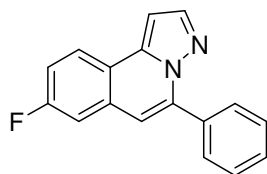
110.1, 112.3, 123.1, 125.6, 126.8, 127.1, 127.3, 128.5, 129.1, 130.6, 132.3, 135.0, 137.3; HRMS calcd. for  $C_{18}H_{14}ClN_2^+$   $[M+H]^+$ : 293.0840, found 293.0847.



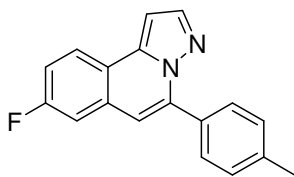
5-Cyclopropyl*H*-pyrazolo[5,1-*a*]isoquinoline **3i**.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  0.91-0.92 (m, 2H), 1.19 (d,  $J = 8.2$  Hz, 2H), 2.67 (t,  $J = 5.4$  Hz, 1H), 6.65 (s, 1H), 7.05 (s, 1H), 7.47-7.49 (m, 2H), 7.61 (d,  $J = 3.2$  Hz, 1H), 8.05 (s, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  6.91, 11.3, 97.7, 106.8, 123.30, 123.38, 126.4, 126.5, 127.6, 129.0, 138.7, 140.6, 140.7; HRMS calcd. for  $C_{14}H_{13}N_2^+$   $[M+H]^+$ : 209.1073, found 209.1086.



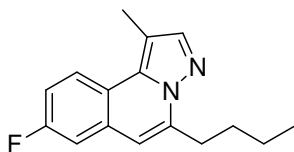
9-Chloro-5-cyclopropyl*H*-pyrazolo[5,1-*a*]isoquinoline **3j**.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  0.91-0.92 (m, 2H), 1.19-1.21 (m, 2H), 2.66-2.67 (m, 1H), 6.60 (s, 1H), 7.02 (s, 1H), 7.42 (d,  $J = 8.2$  Hz, 1H), 7.54 (d,  $J = 8.6$  Hz, 1H), 8.04 (d,  $J = 13.2$  Hz, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  7.03, 11.3, 98.2, 106.1, 122.8, 124.2, 127.3, 127.9, 128.1, 132.1, 137.6, 140.8, 141.1; HRMS calcd. for  $C_{14}H_{11}ClN_2Na^+$   $[M+Na]^+$ : 265.0503, found 265.0520.



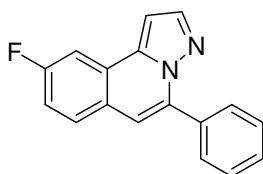
9-Fluoro-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3k**.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  6.96 (s, 1H), 7.01 (s, 1H), 7.23-7.29 (m, 1H), 7.36 (d,  $J = 9.1$  Hz, 1H), 7.51-7.53 (m, 3H), 7.86 (d,  $J = 7.3$  Hz, 2H), 7.99 (s, 1H), 8.06-8.09 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  97.7, 111.8 (d,  $^3J_{CF} = 9.5$  Hz), 112.0 (d,  $^2J_{CF} = 27.7$  Hz), 116.1 (d,  $^2J_{CF} = 23.8$  Hz), 120.8, 125.9 (d,  $^3J_{CF} = 9.5$  Hz), 128.5, 129.5, 129.6, 130.8, 133.5, 139.1, 139.6, 141.2, 162.1 (d,  $^1J_{CF} = 246$  Hz); HRMS calcd. for  $C_{17}H_{11}FN_2Na^+$   $[M+Na]^+$ : 285.0798, found 285.0784.



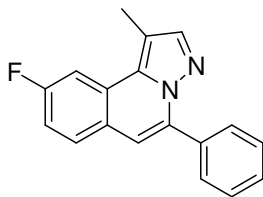
9-Fluoro-5-p-tolyl*H*-pyrazolo[5,1-*a*]isoquinoline **3l**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.46 (s, 3H), 6.94 (s, 1H), 7.01 (s, 1H), 7.14-7.74 (m, 4H), 7.75 (d,  $J = 7.3$  Hz, 2H), 7.98 (s, 1H), 8.06-8.09 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.2, 97.5, 111.2, 111.8 (d,  $^2J_{\text{CF}} = 21.9$  Hz), 115.8 (d,  $^2J_{\text{CF}} = 23.8$  Hz), 120.5, 125.2, 125.7 (d,  $^3J_{\text{CF}} = 8.5$  Hz), 129.1, 129.2, 129.5, 130.5, 130.8 (d,  $^3J_{\text{CF}} = 9.5$  Hz), 138.9, 139.5, 141.0, 161.9 (d,  $^1J_{\text{CF}} = 247.9$  Hz); HRMS calcd. for  $\text{C}_{18}\text{H}_{14}\text{FN}_2^+$   $[\text{M}+\text{H}]^+$ : 277.1136, found 277.1142.



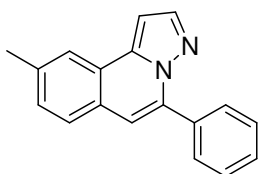
5-Butyl-8-fluoro-1-methyl*H*-pyrazolo[5,1-*a*]isoquinoline **3m**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.99 (t,  $J = 6.8$  Hz, 3H), 1.48-1.53 (m, 2H), 1.81-1.86 (m, 2H), 2.58 (s, 3H), 3.12 (t,  $J = 7.8$  Hz, 2H), 6.68 (s, 1H), 7.22-7.30 (m, 2H), 7.80 (s, 1H), 8.15-8.19 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.6, 13.9, 22.5, 28.8, 30.6, 108.4, 109.3, 111.2 (d,  $^2J_{\text{CF}} = 21.9$  Hz), 114.6 (d,  $^2J_{\text{CF}} = 22.8$  Hz), 121.6, 125.0, 125.1, 131.1, 131.2, 134.3, 140.6, 141.7, 161.2 (d,  $^1J_{\text{CF}} = 245.0$  Hz); HRMS calcd. for  $\text{C}_{16}\text{H}_{18}\text{FN}_2^+$   $[\text{M}+\text{H}]^+$ : 257.1449, found 257.1450.



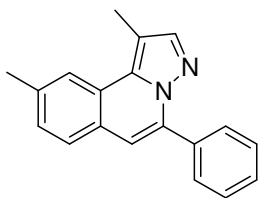
9-Fluoro-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3n**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.01 (s, 1H), 7.04 (s, 1H), 7.49-7.53 (m, 1H), 7.51-7.53 (m, 3H), 7.69-7.74 (m, 2H), 7.86 (d,  $J = 7.3$  Hz, 2H), 8.00 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  98.4, 108.8 (d,  $^2J_{\text{CF}} = 22.8$  Hz), 111.8, 116.6 (d,  $^2J_{\text{CF}} = 23.8$  Hz), 125.3, 125.6, 128.3, 128.5, 129.3, 129.4, 133.5, 137.8, 138.5, 140.8, 161.5 (d,  $^1J_{\text{CF}} = 245.9$  Hz); HRMS calcd. for  $\text{C}_{17}\text{H}_{12}\text{FN}_2^+$   $[\text{M}+\text{H}]^+$ : 263.0979, found 263.0987.



9-Fluoro-1-methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3o**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.63 (s, 3H), 6.93 (s, 1H), 7.22-7.26 (m, 1H), 7.47-7.51 (m, 3H), 7.67-7.70 (m, 1H), 7.81-7.83 (m, 3H), 7.90 (d,  $J = 10.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.6, 108.5, 110.5, 111.6, 115.5 (d,  $^2J_{\text{CF}} = 23.8$  Hz), 125.8, 128.3, 129.0, 129.1, 129.2, 133.7, 141.9, 161.4 (d,  $^1J_{\text{CF}} = 245.9$  Hz); HRMS calcd. for  $\text{C}_{18}\text{H}_{14}\text{FN}_2^+$   $[\text{M}+\text{H}]^+$ : 277.1136, found 277.1138.

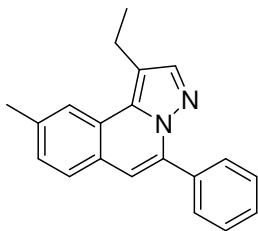


9-Methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3p**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.54 (s, 3H), 6.99 (s, 1H), 7.04 (s, 1H), 7.36 (s, 1H), 7.47-7.51 (m, 3H), 7.61 (d,  $J = 8.2$  Hz, 1H), 7.86-7.90 (m, 3H), 7.97 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.9, 97.7, 112.5, 123.3, 124.2, 127.0, 127.1, 128.4, 129.2, 129.5, 129.6, 134.1, 137.5, 137.7, 139.3, 140.7; HRMS calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 281.1049, found 281.1048.

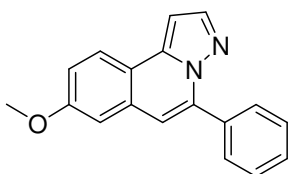


1,9-Dimethyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3q**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.55 (s, 3H), 2.65 (s, 3H), 6.92 (s, 1H), 7.32 (d,  $J = 7.8$  Hz, 1H), 7.45-7.50 (m, 4H), 7.60 (d,  $J = 7.8$  Hz, 1H), 7.78 (s, 1H), 7.82-7.84 (m, 2H), 8.04 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.9, 21.9, 109.8, 112.2, 122.9, 125.6, 126.9, 127.1, 128.2, 128.5, 128.9, 129.3, 134.1, 136.9, 141.7; HRMS calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2^+$   $[\text{M}+\text{H}]^+$ : 273.1386, found 273.1393.

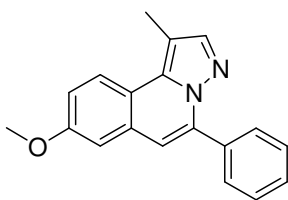




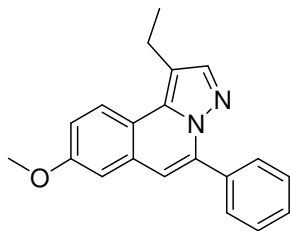
1-Ethyl-9-methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3r**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.45 (t,  $J = 7.3$  Hz, 3H), 2.53 (s, 3H), 3.08 (q,  $J = 7.3$  Hz, 2H), 6.91 (s, 1H), 7.30 (d,  $J = 7.8$  Hz, 1H), 7.45-7.51 (m, 3H), 7.58 (d,  $J = 7.8$  Hz, 1H), 7.81-7.83 (m, 3H), 8.00 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 19.5, 22.0, 112.2, 116.8, 122.9, 125.4, 127.0, 127.2, 128.2, 128.5, 128.9, 129.3, 134.2, 134.3, 137.0, 137.7, 140.0; HRMS calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 309.1362, found 309.1371.



8-Methoxy-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3s**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.93 (s, 3H), 6.97 (d,  $J = 5.9$  Hz, 2H), 7.13-7.25 (m, 2H), 7.49-7.53 (m, 3H), 7.88 (d,  $J = 7.3$  Hz, 2H), 7.96 (s, 1H), 8.03 (d,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  55.4, 96.6, 107.9, 112.2, 117.1, 118.1, 125.1, 128.3, 129.2, 129.3, 130.6, 133.8, 138.8, 139.3, 140.9, 159.2; HRMS calcd. for  $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 275.1179, found 275.1193.

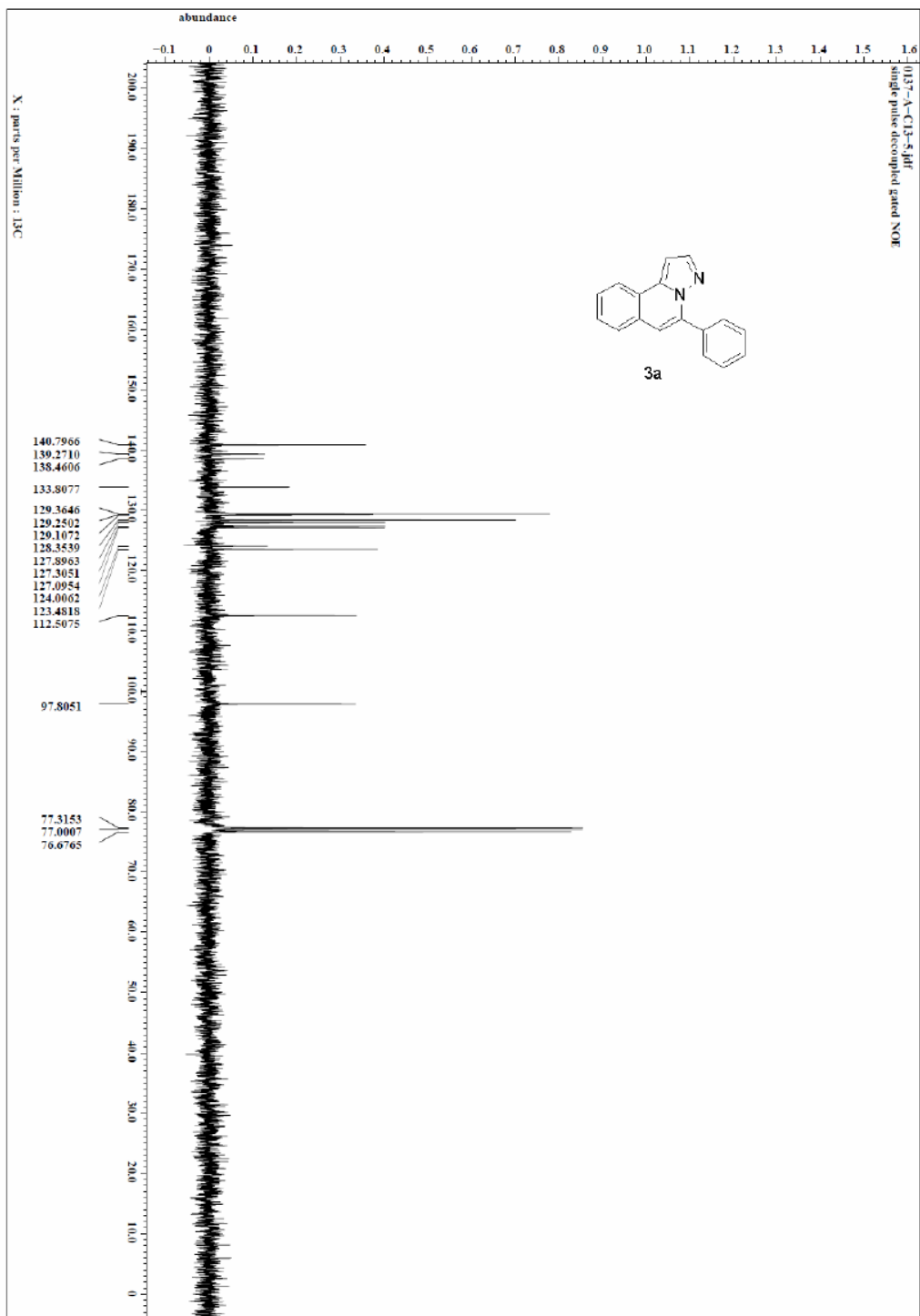


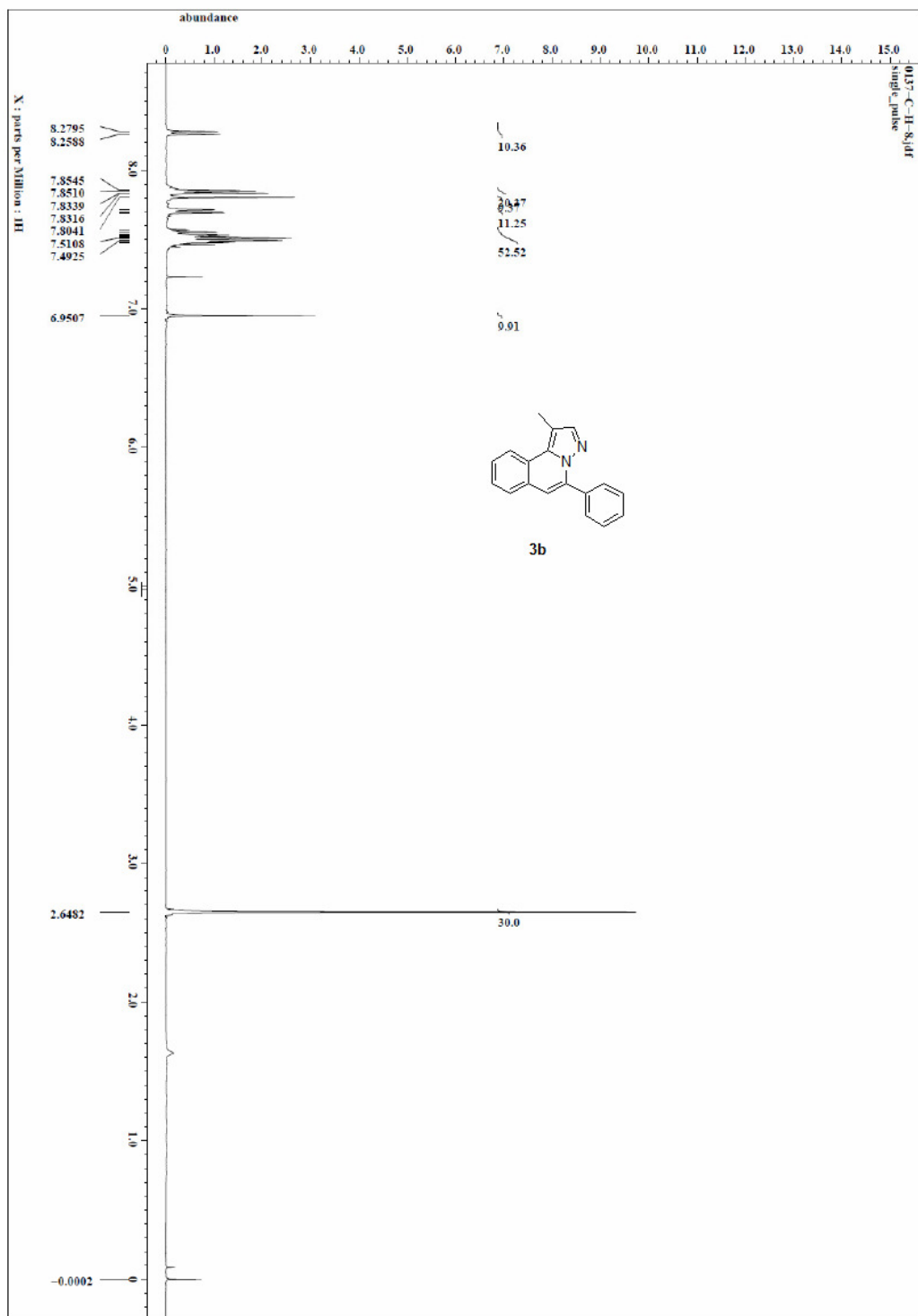
8-Methoxy-1-methyl-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3t**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.63 (s, 3H), 3.39 (s, 3H), 6.91 (s, 1H), 7.14-7.25 (m, 2H), 7.47-7.53 (m, 3H), 7.77 (s, 1H), 7.84 (d,  $J = 7.3$  Hz, 2H), 8.21 (d,  $J = 8.7$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.7, 55.4, 108.3, 108.6, 112.0, 116.5, 119.7, 124.7, 128.3, 129.1, 129.3, 131.0, 133.9, 135.3, 142.1; HRMS calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 289.1335, found 289.1351.

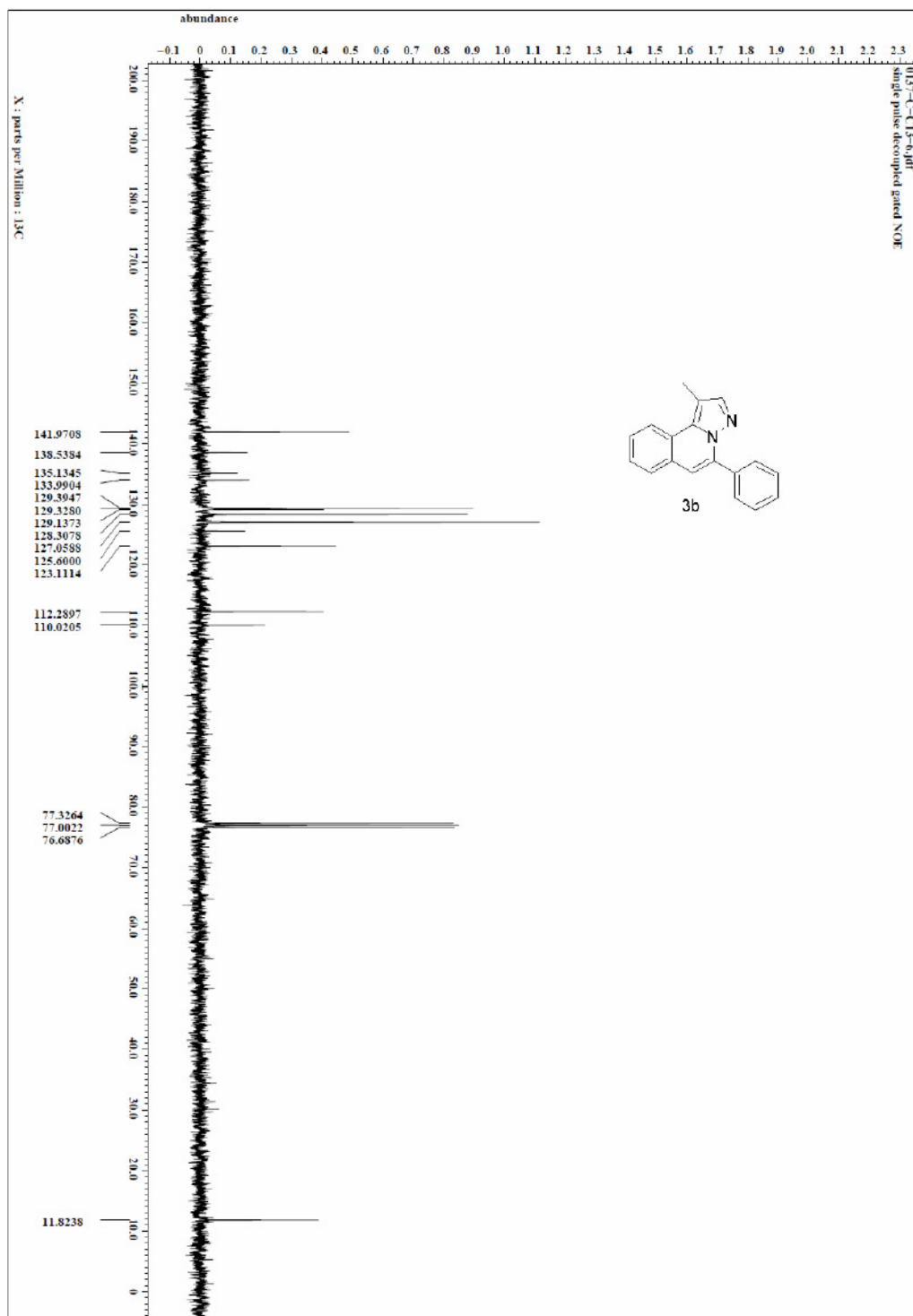


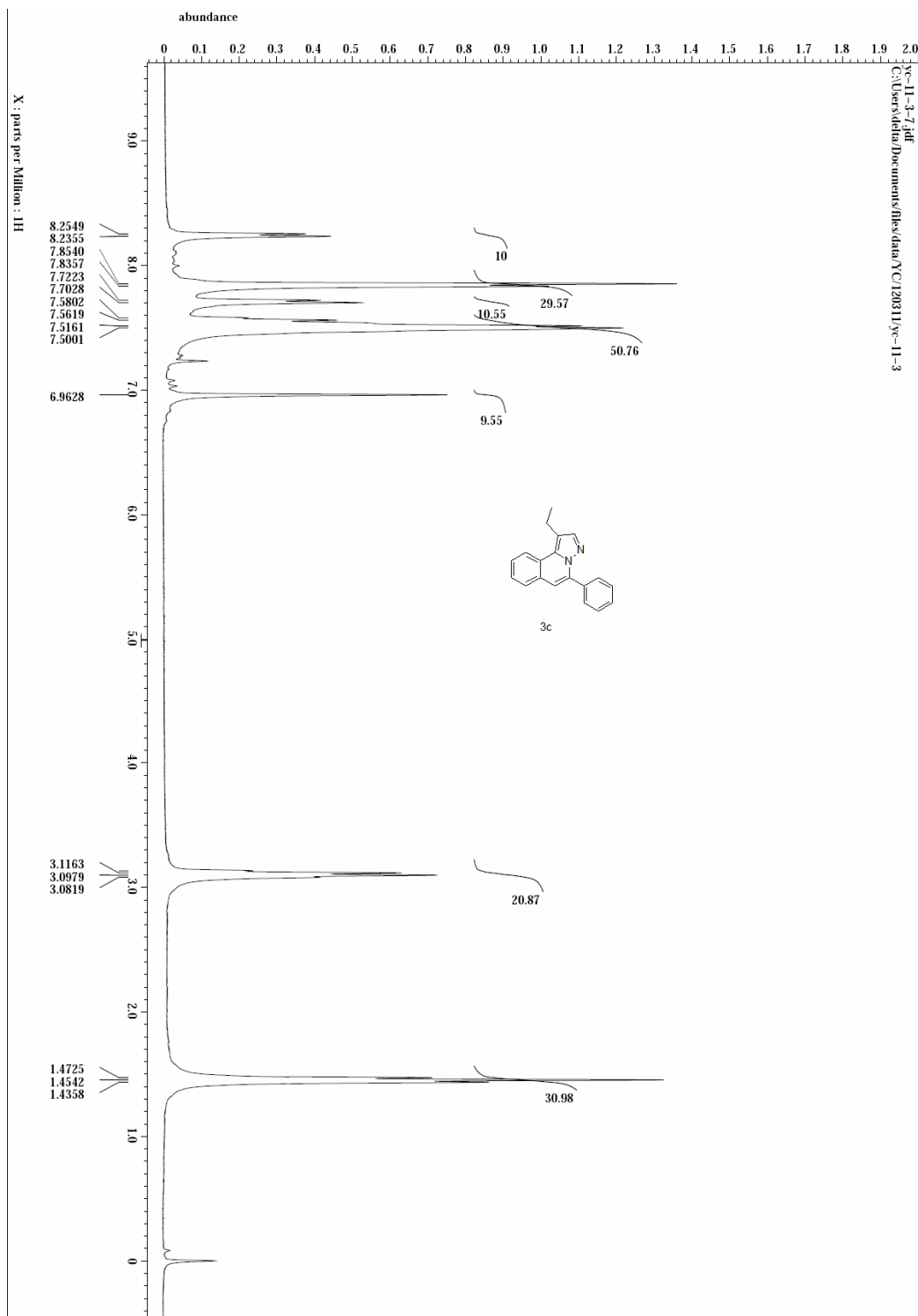
1-Ethyl-8-methoxy-5-phenyl*H*-pyrazolo[5,1-*a*]isoquinoline **3u**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.44 (t,  $J = 7.3$  Hz, 3H), 3.08 (q,  $J = 7.3$  Hz, 2H), 3.92 (s, 3H), 6.91 (s, 1H), 7.13-7.19 (m, 2H), 7.47-7.51 (m, 3H), 7.82-7.85 (m, 3H), 8.17 (d,  $J = 8.7$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 19.3, 55.3, 108.4, 112.0, 115.6, 116.5, 119.5, 124.7, 128.3, 129.1, 129.3, 131.1, 134.0, 138.9, 140.4, 158.5; HRMS calcd. for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 303.1492, found 303.1503.



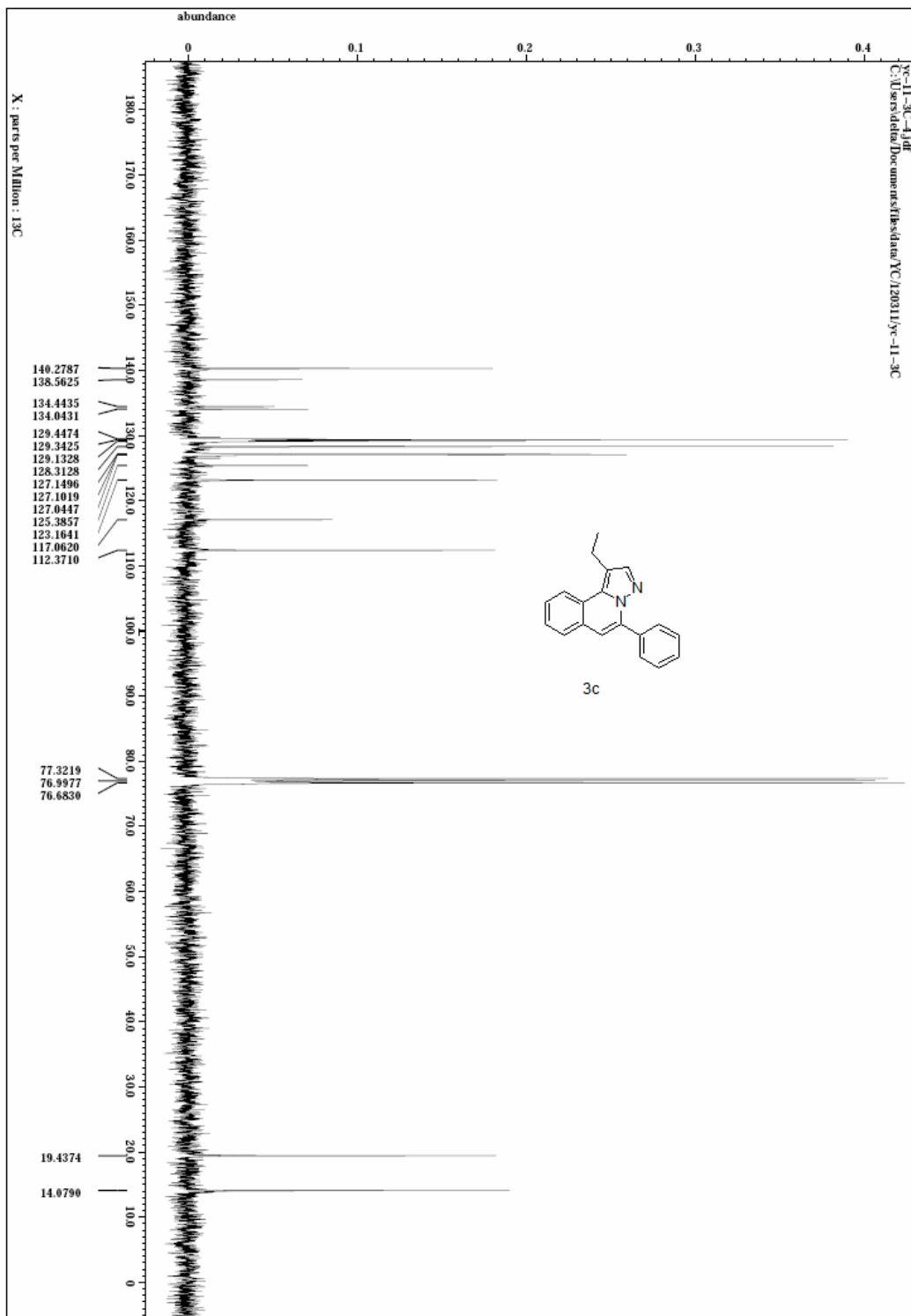




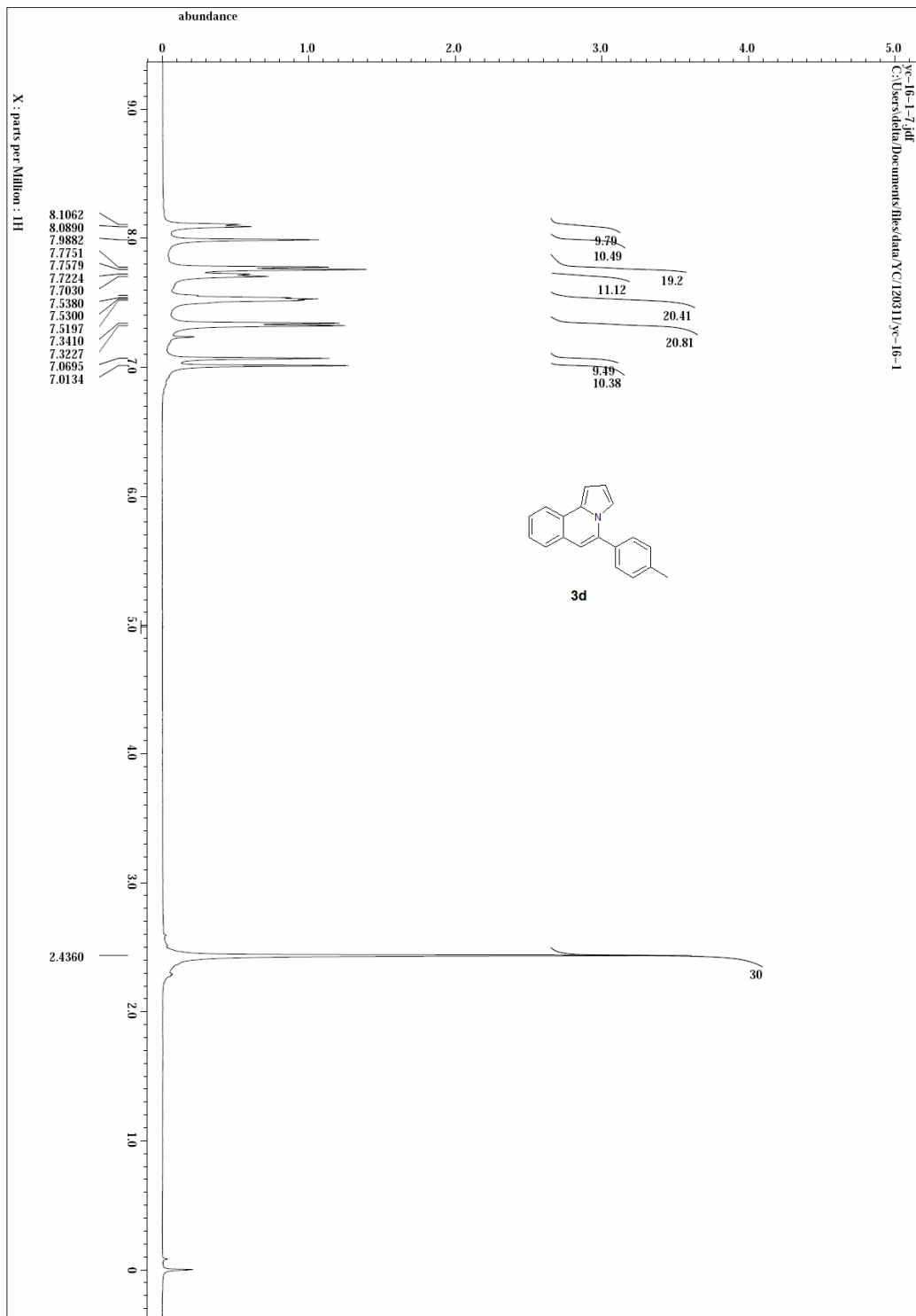




yc-11-3-7.fid  
C:\Users\data\Documents\data\yc\120311\yc-11-3







XC-16-1-7.pdf  
C:\Users\sdclat\Documents\thes\data\YC120811\yc-16-1

