Supporting Information

The Copper-Mediated Cyclization Reaction of Hydrazine with Enediynones Provides Pyrazolo[1,5-\textit{a}]pyridines†

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Table of Contents

P. S1. General procedures
P. S2-20. Data of compound 1a-r and 8a-r.
P. S15-17. X-ray data for 8j
P. S20-24. X-ray data for 9a and 9e
P. S24. References
P. S25-113. Spectra data of compounds
**General procedure for the synthesis of enediynones (1)**

Manganese dioxide (15 mmol) was added to solution of enediynols (6) (1 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was stirred at room temperature for 2 h. The solution was filtered through MgSO₄ and silica gel on cotton plug and washed with dichloromethane. After removal of solvent, the residue was purified by column chromatography to give the products.

**General procedure for the synthesis of vinyl chlorides (4)**

Terminal alkynes (3) (5 mmol), cis-1,2-dichloroethylene (2) (7.5 mmol), Pd(PPh₃)₄ (5 mol %), CuI (5 mol %), and n-BuNH₂ (10 mmol) in ether (10 mL) were stirred at room temperature for 2 h. The saturated aqueous solutions of NH₄Cl and Na₂CO₃ were added subsequently into the reaction mixture and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous MgSO₄. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

**General procedure for the synthesis of pyrazolo[1,5-a]pyridines (8)**

Hydrazine monohydrate (0.3 mmol) was added to a solution of enediynes (0.15 mmol) in CH₃CN (5 ml). The reaction mixture was stirred at 60 °C for 1 h, copper-(I) chloride (0.15 mmol) was then added to the reaction mixture and stirred for an additional 30 h at refluxing temperature under nitrogen. After cooling to room temperature, the solution was filtered through MgSO₄ and silica gel on cotton plug and washed with ethyl acetate. After removal of solvent, the residue was purified by column chromatography to give the products.

**Data of compounds 4**
Compounds 4a~4f, 4j, and 4l, see references [1]~[5].

(Z)-1-(4-chlorobut-3-en-1-yn-1-yl)-2-methylbenzene (4g)
brown liquid; \( R_f = 0.72 \) (n-hexane as eluent);

\(^1\)H NMR (CDCl\(_3\), 300 MHz) : \( \delta \) 7.46 (d, \( J = 7.5 \) Hz, 1H), 7.13-7.25 (m, 3H), 6.45 (d, \( J = 7.5 \) Hz, 1H), 6.13 (d, \( J = 7.2 \) Hz, 1H), 2.5 (s, 3H) ppm; HRMS (EI) calcd. for C\(_{11}\)H\(_9\)Cl 176.0393, found 176.0395.

(Z)-1-(4-chlorobut-3-en-1-yn-1-yl)-3-methylbenzene (4h)
brown liquid; \( R_f = 0.68 \) (n-hexane as eluent);

\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 7.15-7.36 (m, 4H), 6.43 (d, \( J = 7.5 \) Hz, 1H), 6.09 (d, \( J = 7.5 \) Hz, 1H), 2.35 (s, 3H); \(^1^3\)C NMR (CDCl\(_3\). 125MHz) : \( \delta \) 138.1, 132.9, 132.2, 130.1, 129.6, 128.7, 123.2, 123.1, 122.5, 112.1, 21.2 ppm; HRMS (EI) calcd. for C\(_{11}\)H\(_9\)Cl 176.0393, found 176.0395.

(Z)-1-(4-chlorobut-3-en-1-yn-1-yl)-3-methoxybenzene (4k)
brown liquid; \( R_f = 0.67 \) (n-hexane as eluent);

\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 7.24 (d, \( J = 8.0 \) Hz, 1H), 7.10 (d, \( J = 7.5 \) Hz, 1H), 7.02 (s, 1H), 6.91 (dd, \( J = 8.0 \), 2.5 Hz, 1H), 6.45 (d, \( J = 7.5 \) Hz, 1H), 6.09 (d, \( J = 7.5 \) Hz, 1H), 3.82 (s, 3H); \(^1^3\)C NMR (CDCl\(_3\). 125MHz) : \( \delta \) 159.3, 129.4, 128.4, 124.3, 123.6, 116.3, 115.4, 112.0, 97.2, 83.0, 55.3 ppm; HRMS (EI) calcd. for C\(_{11}\)H\(_9\)ClO 192.0342, found 192.0344.

Data of compounds 6

(Z)-1-Phenyltrideca-4-en-2,6-diyn-1-ol (6a)
brown liquid; \( R_f = 0.52 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 7.62 (d, \( J = 8.0 \) Hz, 1H), 7.32-7.40 (m, 3H), 5.88 (td,
$J = 10.5, 2.0$ Hz, 1H), 5.82 (dd, $J = 11.0, 2.0$ Hz, 1H), 5.65 (s, 1H), 2.53 (s, 1H), 2.38
(td, $J = 7.0, 2.0$ Hz, 2H), 1.54 (m, $J = 7.0$ Hz, 2H), 123-1.43 (m, 6H), 0.89 (t, $J = 7.0$
Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz) : $\delta$ 140.39, 128.48(2C), 128.29, 126.78(2C),
121.38, 117.34, 99.55, 95.13, 84.15, 78.06, 65.06, 31.26, 28.54, 28.52, 22.47, 19.74,
14.01 ppm; HRMS (EI) calcd. for C$_{19}$H$_{22}$O 266.1671, found 266.1672.

(Z)-1-Phenylundeca-4-en-2,6-diyn-1-ol (6b)
brown liquid; $R_f = 0.53$ (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 500 MHz) : $\delta$ 7.62 (d, $J = 7.5$ Hz, 2H), 7.32-7.40 (m, 3H), 5.87 (dt,
$J = 11.0, 2.0$ Hz, 1H), 5.82 (dd, $J = 11.0, 2.0$ Hz, 1H), 5.65 (s, 1H), 2.59 (s, 1H), 2.39,
(td, $J = 7.0, 2.0$ Hz, 2H), 1.40-1.56 (m, 4H), 0.90 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR
(CDCl$_3$, 125MHz) : $\delta$ 140.38, 128.47(2C), 128.26, 126.76(2C), 121.33, 117.37, 99.43,
95.15, 84.11, 78.09, 65.03, 30.55, 21.88, 19.38, 13.51 ppm; HRMS (EI) calcd. for C$_{17}$H$_{18}$O 238.1358, found 238.11360.

(Z)-1-phenyldodeca-4-en-2,6-diyn-1-ol (6c)
brown liquid; $R_f = 0.58$ (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 200 MHz) : $\delta$ 7.34-7.63 (m, 5H), 5.77-5.91 (m, 2H), 5.65 (d, $J =$
5.8 Hz, 1H), 2.38 (td, $J = 7.0, 1.6$ Hz, 2H), 2.28 (s, 1H), 1.22-1.62 (m, 6H), 0.88 (t, $J =$
6.8 Hz, 3H) ppm; HRMS (EI) calcd. for C$_{18}$H$_{20}$O 252.1514, found 252.1512.

(Z)-9-Methyl-1-phenyldodeca-4-en-2,6-diyn-1-ol (6d)
brown liquid; $R_f = 0.56$ (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 200 MHz) : $\delta$ 7.59 (dd, $J = 8.0, 2.2$ Hz, 2H), 7.41-7.35 (m, 3H),
5.87-5.84 (m, 2H), 5.65 (s, 1H), 2.28 (dd, $J = 6.6, 1.8$ Hz, 2H), 1.83 (m, 1H), 0.98 (d, $J =$
7.0 Hz, 6H); $^{13}$C NMR (CDCl$_3$, 50MHz) : $\delta$ 143.8, 129.0 (2C), 127.7, 127.2 (2C),
122.1, 118.9, 92.8, 91.1, 84.9, 79.8, 31.8, 28.5, 22.0 (2C) ppm; HRMS (EI) calcd. for C_{17}H_{18}O 238.1358, found 238.1360.

(Z)-8,8-Dimethyl-1-phenylnona-4-en-2,6-diyn-1-ol (6e) brown liquid; \( R_f = 0.57 \) ( \( n \)-hexane/ethyl acetate = 10/1 as eluent );
\(^1\)H NMR (CDCl\(_3\), 300 MHz ) : \( \delta \) 7.60 (d, \( J = 6.6 \) Hz, 2H), 7.32-7.41 (m, 3H), 5.78-5.89 (m, 2H), 5.66 (d, \( J = 5.7 \) Hz, 1H), 2.29 (d, \( J = 6.3 \) Hz, 1H), 1.24 (s, 9H ); \(^{13}\)C NMR (CDCl\(_3\), 50MHz) : \( \delta \) 144.8, 129.0 (2C), 127.6, 127.1 (2C), 118.5, 105.9, 91.1, 84.9, 77.9, 61.8, 31.2 (3C), 28.6 ppm; HRMS (EI) calcd. for C\(_{17}\)H\(_{18}\)O 238.1358, found 238.1359.

(Z)-1,7-Diphenylhepta-4-en-2,6-diyn-1-ol (6f) brown liquid; \( R_f = 0.52 \) ( \( n \)-hexane/ethyl acetate = 10/1 as eluent );
\(^1\)H NMR (CDCl\(_3\), 200 MHz ) : \( \delta \) 7.67-7.29 (m, 10H), 6.11 (d, \( J = 10.8 \) Hz, 1H), 5.95 (dd, \( J = 10.6 \), 1.4 Hz, 1H), 2.04 (s,1H ) ; \(^{13}\)C NMR (CDCl\(_3\), 50MHz) : \( \delta \) 132.3 (2C), 129.0 (2C), 128.5, 128.4 (2C), 127.1 (2C), 122.6, 121.1, 118.9, 94.7, 93.1, 91.1, 84.9, 61.8 ppm; HRMS (EI) calcd. for C\(_{19}\)H\(_{14}\)O 258.1045, found 258.1048.

(Z)-1-phenyl-7-o-tolylhepta-4-en-2,6-diyn-1-ol (6g) brown liquid; \( R_f = 0.51 \) ( \( n \)-hexane/ethyl acetate = 10/1 as eluent );
\(^1\)H NMR (CDCl\(_3\), 400 MHz ) : \( \delta \) 7.61-7.10 (m, 9H), 6.14 (d, \( J = 10.8 \) Hz, 1H), 5.92 (dd, \( J = 10.8 \), 1.6 Hz, 1H), 5.68 (d, \( J = \) Hz, 1H), 2.40 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 140.4, 140.2, 132.1, 129.4, 128.7, 128.6 (2C), 128.4, 126.7 (2C), 125.5, 122.5, 120.7, 118.1, 96.4, 96.3, 90.6, 84.2, 65.2, 20.7 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)O 272.1201, found 272.1203.
(Z)-1-phenyl-7-m-tolylhepta-4-en-2,6-diyn-1-ol (6h)
brown liquid; \( R_f = 0.52 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 7.66-7.13 (m, 9H), 6.10 (d, \( J = 10.8 \) Hz, 1H), 5.94 (dd, \( J = 10.8, 2 \) Hz, 1H), 5.70 (s, 1H), 2.30 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 140.3, 137.9, 132.3, 129.6, 128.9, 1128.6 (2C), 128.3, 128.2, 126.7 (2C), 122.5, 120.7, 118.4, 97.7, 96.3, 86.4, 84.1, 65.2, 21.1 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)O 272.1201, found 272.1202.

(Z)-7-(2-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-ol (6j)
brown liquid; \( R_f = 0.53 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 7.63 (dd, \( J = 7.5, 2.5 \) Hz, 2H), 7.29-7.36 (m, 4H), 6.87-6.91 (m, 2H), 6.17 (d, \( J = 10.5 \) Hz, 1H), 5.93 (dd, \( J = 11.0, 2.0 \) Hz, 1H), 5.69 (d, \( J = 3.0 \) Hz, 1H), 3.83 (s, 3H), 2.58 (d, \( J = 5.5 \) Hz, 1H); \(^13\)C NMR (CDCl\(_3\), 125MHz) : \( \delta \) 159.87, 140.35, 133.99, 130.28, 128.57(2C), 128.30, 126.81(2C), 121.03, 120.60, 118.10, 112.09, 110.83, 96.49, 93.96, 90.90, 84.42, 65.16, 55.90 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)O\(_2\) 288.1150, found 288.1151.

(Z)-7-(4-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-ol (6l)
brown liquid; \( R_f = 0.54 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 200 MHz) : \( \delta \) 7.62-7.67 (m, 2H), 7.30-7.36 (m, 2H), 6.79-6.85 (m, 2H), 6.09 (d, \( J = 10.6 \) Hz, 1H), 5.90 (dd, \( J = 11.0, 1.8 \) Hz, 1H), 5.70 (d, \( J = 4.6 \) Hz, 1H), 3.81 (s, 3H), 2.39 (d, \( J = 6.2 \) Hz, 1H) ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)O\(_2\) 288.1150, found 288.1152.

(Z)-7-(4-nitrophenyl)-1-phenylhepta-4-en-2,6-diyn-1-ol (6m)
Yellow solid; m.p.: 88-90 °C \( R_f = 0.42 \) (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 8.14 (d, $J = 9$ Hz, 2H), 7.60-7.64 (m, 2H), 7.45 (d, $J = 8.7$ Hz, 3H), 7.34-7.36 (m, 3H), 6.09 (m, 2H), 5.71 (d, $J = 5.4$ Hz, 1H), 2.34 (d, $J = 4.2$ Hz, 1H) ppm; HRMS (EI) calcd. for C$_{19}$H$_{13}$NO$_3$ 303.0895, found 303.0897.

(Z)-7-(4-hexylphenyl)-1-(4-methoxyphenyl)hepta-4-en-2,6-diyn-1-ol (6n)
brown liquid; $R_f = 0.58$ (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 7.54 (d, $J = 8.7$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 5.79-5.89 (m, 2H), 5.60 (d, $J = 5.4$ Hz), 3.81 (s, 3H), 2.38 (td, $J = 7.2$, 1.8 Hz, 2H), 2.14 (d, $J = 6.3$ Hz, 1H), 1.23-1.55 (m, 8H), 0.87 (t, $J = 6.9$ Hz, 3H) ppm; HRMS (EI) calcd. for C$_{20}$H$_{22}$O$_2$ 296.1776, found 296.1777.

(Z)-1-(4-methoxyphenyl)-7-phenylhepta-4-en-2,6-diyn-1-ol (6o)
brown liquid; $R_f = 0.55$ (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 7.56 (d, $J = 8.7$ Hz, 2H), 7.28-7.41 (m, 5H), 6.82 (d, $J = 8.7$ Hz, 2H), 6.10 (d, $J = 10.8$, 1H), 5.96 (dd, $J = 10.8$, 1.5 Hz, 1H), 3.76 (s, 3H), 2.19 (d, $J = 6$ Hz, 1H) ppm; HRMS (EI) calcd. for C$_{20}$H$_{16}$O$_2$ 288.1150, found 288.1152.

(Z)-1,7-bis(4-methoxyphenyl)hepta-4-en-2,6-diyn-1-ol (6p)
brown liquid; $R_f = 0.53$ (n-hexane/ethyl acetate = 10/1 as eluent);
$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 7.56 (d, $J = 6.9$ Hz, 2H), 7.32 (d, $J = 6.3$, 2H), 6.83 (m, 4H), 6.08 (d, $J = 10.8$ Hz, 1H), 5.90 (dd, $J = 10.8$, 1.8 Hz, 1H), 5.64 (d, $J = 5.7$ Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.24 (d, $J = 6.3$ Hz, 1H) ppm; HRMS (EI) calcd. for C$_{2}$H$_{18}$O$_3$ 318.1256, found 318.1257.

(Z)-4-(7-hydroxy-7-(4-methoxyphenyl)hepta-3-en-1,5-diyn-1-yl)benzonitrile (6q)
brown liquid; \( R_f = 0.50 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 300 MHz) : \( \delta \) 7.50-7.55 (m, 4H), 7.39 (d, \( J = 8.4 \) Hz, 2H), 6.84 (d, \( J = 8.7 \) Hz, 2H), 6.02-6.11 (m, 2H), 5.64 (d, \( J = 5.7 \) Hz, 1H), 3.79 (s, 3H), 2.23 (d, \( J = 5.4 \) Hz, 1H) ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{21}\)F\(_3\)O 334.1544, found 334.1546.

**Data of compounds 1**

**\((Z)-1\)-Phenyltrideca-4-en-2,6-diyn-1-one (1a)**

brown liquid; \( R_f = 0.62 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.23 (\( J = 7.8 \)Hz, 2H), 7.66-7.43 (m, 3H), 6.21 (dt, \( J = 10.6, 2.2 \) Hz, 1H), 5.98 (d, \( J = 10.6 \) Hz, 1H), 2.48 (td, \( J = 6.8, 2.2 \) Hz, 2H), 1.66-1.20 (m, 8H), 0.85 (t, \( J = 6.6 \) Hz, 3H) ; \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 177.9, 135.2, 134.7, 129.9 (2C), 128.5 (2C), 122.8, 117.3, 109.1, 93.8, 89.9, 30.9, 30.2, 28.1, 26.3, 22.2, 14.1 ppm; HRMS (EI) calcd. for C\(_{19}\)H\(_{20}\)O 264.1514, found 264.1516.

**\((Z)-1\)-Phenylundeca-4-en-2,6-diyn-1-one (1b)**

brown liquid; \( R_f = 0.62 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.24 (d, \( J = 7.8 \) Hz, 2H), 7.61 (t, \( J = 7.2 \)Hz, 2H), 7.47 (t, \( J = 7.0 \)Hz, 1H), 6.19 (dt, \( J = 10.6, 2.2 \) Hz, 1H), 5.98 (d, \( J = 10.6 \) Hz, 1H), 2.47 (td, \( J = 8.8, 1.8 \) Hz, 2H), 1.65-1.37 (m, 4H), 0.87 (t, \( J = 6.8 \) Hz, 3H) ; \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 177.5, 135.1, 134.6, 129.7 (2C), 128.4 (2C), 126.8, 115.6, 109.3, 93.8, 89.9, 31.2, 21.5, 18.9, 14.8 ppm; HRMS (EI) calcd. for C\(_{17}\)H\(_{16}\)O 236.1201, found 236.1200.

**\((Z)-9\)-Methyl-1-phenyldeca-4-en-2,6-diyn-1-one (1d)**

Yellow green liquid; \( R_f = 0.66 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.24 (d, \( J = 7.8 \) Hz, 2H), 7.61 (t, \( J = 7.2 \) Hz, 2H), 7.47 (t, \( J = 7.0 \) Hz, 1H), 6.18 (dt, \( J = 10.6, 2.2 \) Hz, 1H), 5.98 (d, \( J = 10.6 \) Hz, 1H), 2.36 (dd, \( J = 7.0 \) Hz, 1H), 2.23 (d, \( J = 7.0 \) Hz, 1H), 6.02-6.11 (m, 2H), 5.64 (d, \( J = 5.7 \) Hz, 1H), 3.79 (s, 3H), 2.23 (d, \( J = 5.4 \) Hz, 1H) ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{21}\)F\(_3\)O 334.1544, found 334.1546.
8.8, 2.2 Hz, 2H), 1.87 (m, J = 6.6 Hz, 1H), 0.98 (d, J = 6.6 Hz, 6H) ; $^{13}$C NMR (CDCl$_3$, 100MHz) : $\delta$ 177.8, 136.7, 134.6, 129.8 (2C), 128.5 (2C), 126.8, 115.7, 102.1, 92.1, 90.1, 79.1, 29.1, 28.1, 22.0 (2C) ppm; HRMS (EI) cacld. for 236.1201, found 236.1200; Chemical Formula: C$_{17}$H$_{16}$O

**(Z)-8,8-Dimethyl-1-phenylnona-4-en-2,6-diyn-1-one (1e)**

brown liquid; $R_f$ = 0.62 ( n-hexane/ethyl acetate = 20/1 as eluent ); $^1$H NMR (CDCl$_3$, 400 MHz ) : $\delta$ 8.23 (d, J = 7.4Hz, 2H), 7.61-7.47 (m, 3H), 6.17 (d, J = 10.6 Hz, 1H), 5.98 (d, J = 10.6 Hz, 1H), 1.30 (s, 9H) ; $^{13}$C NMR (CDCl$_3$, 100MHz) : $\delta$ 177.6, 135.1, 134.6, 129.7 (2C), 128.4 (2C), 124.3, 115.5, 103.9, 93.8, 89.9, 78.9, 31.2 (3C), 28.6ppm; HRMS (EI) calcd. for C$_{17}$H$_{16}$O 236.1201, found 236.1199.

**(Z)-1,7-Diphenylhepta-4-en-2,6-diyn-1-one (1f)**

brown liquid; $R_f$ = 0.55 ( n-hexane/ethyl acetate = 20/1 as eluent ); $^1$H NMR (CDCl$_3$, 400 MHz ) : $\delta$ 8.25 (d, J = 7.8 Hz, 2H), 7.55-7.30 (m, 8H), 6.42 (d, J = 10.6 Hz, 1H), 6.12 (d, J = 10.6 Hz, 1H) ; $^{13}$C NMR (CDCl$_3$, 100MHz) : $\delta$ 177.9, 135.6, 134.1, 130.1 (2C), 129.7 (2C), 129.3 (2C), 128.2 (2C), 127.8, 124.5, 117.3, 112.5, 109.7, 93.8 ppm; HRMS (EI) calcd. for C$_{19}$H$_{12}$O 256.0888, found 256.0891.

**(Z)-1-phenyl-7-o-tolylhepta-4-en-2,6-diyn-1-one (1g)**

brown liquid; $R_f$ = 0.54 ( n-hexane/ethyl acetate = 20/1 as eluent ); $^1$H NMR (CDCl$_3$, 400 MHz ) : $\delta$ 8.23 (d, J = 7.2 Hz, 2H), 7.54-7.22 (m, 7H), 6.46 (d, J = 10.8 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 2.43 (s, 3H) ; $^{13}$C NMR (CDCl$_3$, 100MHz) : $\delta$177.7, 140.8, 136.6, 134.0, 132.3, 129.7 (2C), 129.6, 129.3, 128.6, 128.5 (2C), 125.6, 116.2, 99.5, 92.9, 91.0, 90.3, 20.7 ppm; HRMS (EI) calcd. for C$_{13}$H$_{14}$O 270.1045, found 270.1046.
(Z)-1-phenyl-7-m-tolylhepta-4-en-2,6-diyn-1-one (1h)

brown liquid; \( R_f = 0.58 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.29 (d, \( J = 7.2 \) Hz, 2H), 7.55 (t, \( J = 7.2 \) Hz, 1H), 7.36-7.18 (m, 6H), 6.42 (d, \( J = 10.8 \) Hz, 1H), 6.13 (d, \( J = 10.8 \) Hz, 1H), 2.30 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 177.7, 138.1, 136.7, 134.0, 132.4, 130.2, 129.7 (2C), 129.0, 128.6, 128.5 (2C), 128.3, 126.3, 116.6, 100.9, 92.9, 89.7, 86.4, 21.1 ppm; HRMS (EI) calcd. for C\(_{12}\)H\(_{14}\)O 270.1045, found 270.1043.

(Z)-1-phenyl-7-(p-tolyl)hepta-4-en-2,6-diyn-1-one (1i)

brown solid; m.p.: 46-48 °C \( R_f = 0.62 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.27 (d, \( J = 7.2 \) Hz, 2H), 7.56 (t, \( J = 7.2 \) Hz, 1H), 7.47-7.34 (m, 4H), 6.86 (d, \( J = 8.4 \) Hz, 2H), 6.40 (d, \( J = 10.8 \) Hz, 1H), 6.06 (d, \( J = 10.8 \) Hz, 1H), 3.82 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 177.7, 160.4, 136.7, 133.9, 133.5 (2C), 129.6 (2C), 129.4, 128.7, 129.5 (2C), 126.6, 115.6, 114.1 (2C), 101.2, 92.8, 90.1, 86.0, 55.3ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{14}\)O\(_2\) 286.0994, found 286.0991.

(Z)-7-(2-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1j)

brown solid; m.p.: 40-42 °C \( R_f = 0.56 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.28 (d, \( J = 7.2 \) Hz, 2H), 7.53-7.27 (m, 5H), 6.90 (d, \( J = 8.4 \) Hz, 1H), 6.96 (td, \( J = 7.4, 0.8 \) Hz, 1H), 6.50 (d, \( J = 10.6 \) Hz, 1H), 6.13 (d, \( J = 10.8 \) Hz, 1H), 3.77 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 177.8, 160.2, 136.7, 133.9, 130.9, 129.8 (2C), 128.4 (2C), 127.8, 126.5, 120.5, 116.2, 111.4, 110.6, 97.2, 91.3, 90.7, 90.0, 55.6 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{14}\)O\(_2\) 286.0994, found 286.0992.

(Z)-7-(3-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1k)

brown solid; m.p.: 48-50 °C \( R_f = 0.52 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1\)H
NMR (CDCl$_3$, 500 MHz) : $\delta$ 8.27 (dd, $J = 8.5$, 1.5 Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.28-7.24 (m, 2H), 7.13 (dt, $J = 7.5$, 1 Hz, 1H), 7.05 (dd, $J = 2.5$, 1.5 Hz, 2H), 6.94 (ddd, $J = 8$, 2.5, 1 Hz, 1H), 6.41 (d, $J = 10.5$, 1H), 6.13 (d, $J = 10.5$, 1H), 3.75 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz) : $\delta$ 177.7, 159.3, 136.7, 134.0, 129.7 (2C), 129.5, 128.6 (2C), 126.1, 124.4, 123.1, 117.0, 116.4, 116.2, 100.5, 93.0, 89.6, 86.5, 55.2 ppm; HRMS (EI) calcd. for C$_{20}$H$_{14}$O$_2$ 286.0994, found 286.0991.

(Z)-7-(4-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1l)
brown solid; m.p.: 46-48 °C $R_f$ = 0.56 (n-hexane/ethyl acetate = 20/1 as eluent); $^1$H NMR (CDCl$_3$, 400 MHz) : $\delta$ 8.27 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.34-7.47 (m, 5H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.40 (d, $J = 10.8$ Hz, 1H), 6.06 (d, $J = 10.8$ Hz, 1H), 3.82 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz) : $\delta$ 177.8, 160.5, 136.7, 133.9, 133.5(2C), 129.6(2C), 129.4, 128.5(2C), 126.6, 115.6, 114.1(2C), 101.2, 92.8, 90.1, 86.7, 55.3 ppm; HRMS (EI) calcd. for C$_{20}$H$_{14}$O$_2$ 286.0994, found 286.0992.

(Z)-7-(4-nitrophenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1m)
yellow solid; m.p.: 68-70 °C $R_f$ = 0.48 (n-hexane/ethyl acetate = 20/1 as eluent); $^1$H NMR (CDCl$_3$, 500 MHz) : $\delta$ 8.20-8.24 (m, 4H), 7.59-7.67 (m, 3H), 7.41 (t, $J = 7.5$ Hz, 2H), 6.43 (d, $J = 10.5$ Hz, 1H), 6.24 (d, $J = 10.5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125MHz) : $\delta$ 177.5, 147.6, 136.6, 134.3, 132.7(2C), 129.6(2C), 128.9, 128.6(2C), 124.9, 123.7(2C), 119.1, 97.5, 93.7, 90.9, 88.8 ppm; HRMS (EI) calcd. for C$_{19}$H$_{11}$NO$_3$ 301.0379, found 301.0380.

(Z)-1-(4-methoxyphenyl)trideca-4-en-2,6-diyn-1-one (1n)
brown liquid; $R_f$ = 0.58 (n-hexane/ethyl acetate = 20/1 as eluent); $^1$H NMR (CDCl$_3$, 500 MHz) : $\delta$ 8.22 (d, $J = 9$ Hz, 2H), 6.94 (d, $J = 9$ Hz, 2H), 6.14 (dt, $J = 10.5$, 2.5 Hz,
1H), 5.98 (d, J = 11 Hz, 1H), 3.88 (s,3H), 2.46 (td, J = 7.0, 2.0 Hz, 2H0, 1.58 (m, J = 7.5 Hz, 2H), 1.23-1.43 (m, 6H), 0.85 (t, J = 7.0 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz) : δ 176.4, 164.3, 132.2(2C), 130.3, 126.3, 115.9, 113.7(2C), 102.7, 92.1, 89.3, 78.3, 55.5, 31.3, 28.6, 28.4, 22.4, 19.9, 13.9 ppm; HRMS (EI) calcd. for C$_{20}$H$_{22}$O$_2$ 294.1620, found 294.1621.

(Z)-1-(4-methoxyphenyl)-7-phenylhepta-4-en-2,6-diyn-1-one (1o)
brown liquid; $R_f$ = 0.55 ( n-hexane/ethyl acetate = 20/1 as eluent ); $^1$H NMR (CDCl$_3$, 300 MHz ) : δ 8.24 (d, J = 9.0 Hz, 2H), 7.32-7.55 (m, 5H), 6.76 (d, J = 9.0 Hz, 1H), 6.39 (d, J = 10.5 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 3.80 (s, 3H) ppm; HRMS (EI) calcd. for C$_{20}$H$_{14}$O$_2$ 286.0994, found 286.0992.

(Z)-1,7-bis(4-methoxyphenyl)hepta-4-en-2,6-diyn-1-one (1p)
orange liquid; $R_f$ = 0.48 ( n-hexane/ethyl acetate = 20/1 as eluent ); $^1$H NMR (CDCl$_3$, 500 MHz ) : δ 8.24 (d, J = 9 Hz, 2H), 7.48 (d, J = 9 Hz, 2H), 6.88 (d, J = 9 Hz, 2H), 6.79 (d, J = 9 Hz, 2H), 6.38 (d, J = 10.5 Hz, 1H), 6.07 (d, J = 10.5 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125MHz) : δ176.4, 164.3, 160.4, 133.6 (2C), 132.1 (2C), 130.2, 126.1, 116.1, 114.4, 114.1 (2C), 113.8 (2C), 100.7, 93.0, 89.3, 86.1, 55.4, 55.3ppm; HRMS (EI) calcd. for C$_{21}$H$_{16}$O$_3$ 316.1099, found 316.1099

(Z)-4-(7-(4-methoxyphenyl)-7-oxohepta-3-en-1,5-diynyl)benzonitrile (1q)
Yellow solid; m.p.: 56-58 °C $R_f$ = 0.62 ( n-hexane/ethyl acetate = 20/1 as eluent ); $^1$H NMR (CDCl$_3$, 500 MHz ) : δ 8.18 (d, J = 9 Hz, 2H), 7.64-7.59 (m, 4H), 6.83 (d, J = 9 Hz, 2H), 6.38 (d, J = 10.5 Hz, 1H), 6.20 (d, J = 10.5 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz) : δ176.1, 164.5, 132.4 (2C), 132.1 (2C), 132.0 (2C), 130.0, 127.1, 124.5, 119.0, 118.2, 113.8 (2C), 112.4, 97.6, 93.8, 90.4, 88.2, 55.5 ppm; HRMS (EI)
calcd. for C_{21}H_{13}NO_{2} 311.0946, found 311.0946.

(Z)-1-(4-(trifluoromethyl)phenyl)trideca-4-en-2,6-diyn-1-one (1r)
brown liquid; \( R_f = 0.57 \) (n-hexane/ethyl acetate = 20/1 as eluent); \(^1^H \text{NMR (CDCl}_3\), 500 MHz :} \( \delta \) 88.37 (d, \( J = 8 \) Hz, 2H), 7.75 (d, \( J = 8 \) Hz, 2H), 6.23 (dt, \( J = 11, 2.5 \) Hz), 6.01 (d, \( J = 11 \)Hz), 2.47 (td, \( J = 7.5, 2.5 \) Hz, 2H), 1.59 (quintet, \( J = 7.5 \) Hz, 2H), 1.40 (quintet, \( J = 7.5 \) Hz, 2H), 1.26 (m, 4H), 0.85 (t, \( J = 7 \) Hz, 3H); \(^{13}\text{C NMR (CDCl}_3\), 125MHz} : \( \delta \) 176.4, 139.3, 130.0 (2C), 127.8, 125.5 (quartet, \( J = 3.6 \) Hz), 115.3, 103.7, 91.5, 91.4, 78.3, 31.2, 28.6, 28.4, 22.4, 20.0, 13.9 ppm; HRMS (EI) calcd. for C_{20}H_{19}F_{3}O 332.1388, found 332.1391.

Data of compound 8a-8r

7-Hexyl-2-phenylpyrazolo[1,5-a]pyridine (8a)
brown liquid; \( R_f = 0.69 \) (n-hexane/ethyl acetate = 10/1 as eluent); \(^1^H \text{NMR (CDCl}_3\), 400 MHz :} \( \delta \) 8.03 (dt, \( J = 7.2, 1.2 \) Hz, 2H), 7.48-7.35 (m, 4H), 7.05 (dd, \( J = 9.2, 7.0 \) Hz, 1H), 6.28 (s, 1H), 6.58 (dt, \( J = 6.8, 0.8 \) Hz, 1H), 3.22 (t, \( J = 7.6 \) Hz, 2H), 1.92 (m, 2H), 1.52-1.25 (m, 8H), 0.93 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\text{C NMR (CDCl}_3\). 50MHz} : \( \delta \) 152.6, 128.6 (2C), 128.1, 126.5 (3C), 123.3, 115.3, 109.6, 93.6, 31.6, 30.9, 29.6, 29.1, 26.1, 22.6, 14.8; \(^{13}\text{C NMR (CDCl}_3\), 100MHz} : \( \delta \) 152.5, 142.2, 133.7, 128.6 (2C), 128.1, 126.5 (2C), 123.2, 115.2, 109.5, 31.6, 30.9, 29.1, 26.1, 22.5, 14.0 ppm; HRMS (EI) calcd. for C_{10}H_{22}N_{2} 278.1783, found 278.1780.

7-Butyl-2-phenylpyrazolo[1,5-a]pyridine (8b)
brown liquid; \( R_f = 0.67 \) (n-hexane/ethyl acetate = 10/1 as eluent); \(^1^H \text{NMR (CDCl}_3\), 400 MHz :} \( \delta \) 8.11 (dt, \( J = 8.4, 1.8 \) Hz, 2H), 7.53-7.36 (m, 4H), 7.16 (dd, \( J = 9.0, 7.0 \) Hz, 1H), 6.80 (s, 1H), 6.65 (dt, \( J = 6.8, 0.8 \) Hz, 1H), 3.20 (t, \( J = 7.6 \) Hz, 2H), 1.90 (m,
\( J = 7.2 \text{ Hz}, 2H \), 1.60 (m, \( J = 7.0 \text{ Hz}, 2H \)), 1.02 (t, \( J = 7.4 \text{Hz}, 3H \) ); \( ^{13} \text{C NMR (CDCl}_3, 100\text{MHz}) : \delta \) 152.5, 142.2, 142.0 133.7, 128.6 (2C), 128.1, 126.5 (2C), 122.1, 116.5, 109.5, 93.4, 31.5, 31.4, 22.3, 14.1 ppm; HRMS (EI) calcd. for \( \text{C}_{17}\text{H}_{18}\text{N}_2 \) 250.1470, found 250.1469.

**7-pentyl-2-phenylpyrazolo[1,5-a]pyridine (8c)**

brown liquid; \( R_f = 0.61 \) ( n-hexane/ethyl acetate = 10/1 as eluent ); \( ^{1} \text{H NMR (CDCl}_3, 400 \text{ MHz)} : \delta \) 8.04 (dt, \( J = 7.2, 1.6 \text{ Hz}, 2H \)), 7.48-7.34 (m, 4H), 7.07 (dd, \( J = 8.8, 6.8 \text{ Hz}, 1H \)), 6.82 (s, 1H), 6.59 (dt, \( J = 6.8, 0.8 \text{ Hz}, 1H \)) 3.24 (t, \( J = 8 \text{ Hz}, 2H \)), 1.96 (q, \( J = 7.6 \text{ Hz}, 2H \)), 1.50 (m, 4H), 0.97 (t, \( J = 6.8 \text{ Hz}, 3H \) ); \( ^{13} \text{C NMR (CDCl}_3, 100\text{MHz)} : \delta \) 152.5, 142.2, 142.0, 133.7, 128.6 (2C), 128.1, 126.5 (2C), 123.2, 115.2, 109.5, 93.6, 31.6, 30.9, 25.8, 22.4, 14.0 ppm; HRMS (EI) calcd. for \( \text{C}_{18}\text{H}_{20}\text{N}_2 \) 264.1626, found 264.1629.

**7-Isobutyl-2-phenylpyrazolo[1,5-a]pyridine (8d)**

brown liquid; \( R_f = 0.58 \) ( n-hexane/ethyl acetate = 10/1 as eluent ); \( ^{1} \text{H NMR (CDCl}_3, 400 \text{ MHz)} : \delta \) 8.02 (dt, \( J = 6.8, 1.6 \text{ Hz}, 2H \)), 7.49-7.30 (m, 4H), 7.05 (dd, \( J = 8.8, 6.8 \text{ Hz}, 1H \)), 6.81 (s, 1H), 6.55 (dt, \( J = 7.0, 0.8 \text{ Hz}, 1H \)), 3.08 (d, \( J = 7.0 \text{ Hz}, 2H \)), 2.50 (m, \( J = 6.8 \text{ Hz}, 1H \)), 1.03 (d, \( J = 6.6 \text{ Hz}, 6H \) ); \( ^{13} \text{C NMR (CDCl}_3, 100\text{MHz)} : \delta \) 152.4, 142.1, 141.1, 128.6 (2C), 128.1, 126.5 (2C), 123.1, 115.4, 110.9, 93.5, 40.4, 25.3, 22.7 (2C) ppm; HRMS (EI) calcd. for \( \text{C}_{18}\text{H}_{20}\text{N}_2 \) 250.1470, found 250.1469.

**7-tert-butyl-2-phenylpyrazolo[1,5-a]pyridine (8e)**

brown liquid; \( R_f = 0.60 \) ( n-hexane/ethyl acetate = 10/1 as eluent ); \( ^{1} \text{H NMR (CDCl}_3, 400 \text{ MHz)} : \delta \) 8.03 (dt, \( J = 6.8, 1.6 \text{ Hz}, 2H \)), 7.47-7.33 (m, 4H), 7.04 (dd, \( J = 8.8, 6.8 \text{ Hz}, 1H \)), 6.80 (s,1H), 6.65 (dd, \( J = 7.2, 1.2 \text{ Hz}, 1H \)), 1.68 (s, 9H) ; \( ^{13} \text{C NMR (CDCl}_3, 100\text{MHz)} : \delta \) 152.5, 142.2, 142.0, 133.7, 128.6 (2C), 128.1, 126.5 (2C), 123.2, 115.4, 110.9, 93.5, 40.4, 25.3, 22.7 (2C) ppm; HRMS (EI) calcd. for \( \text{C}_{18}\text{H}_{20}\text{N}_2 \) 250.1470, found 250.1469.
100MHz): δ 152.5, 142.2, 141.1, 133.7, 128.6 (2C), 128.1, 126.5 (2C), 122.1, 115.6, 109.5, 93.5, 31.7, 30.3 (3C) ppm; HRMS (EI) calcd. for C_{17}H_{18}N_{2} 250.1470, found 250.1467.

2,7-Diphenylpyrazolo[1,5-a]pyridine (8f)
brown liquid; $R_f = 0.52$ (n-hexane/ethyl acetate = 10/1 as eluent); $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.10-8.02 (m, 4H), 7.56-7.35 (m, 7H), 7.18 (dd, $J = 8.8, 7.0$ Hz, 1H), 6.91 (s, 1H), 6.84 (dd, $J = 7.0$, 1.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100MHz): δ 152.7, 142.7, 140.2, 133.6, 133.4, 129.3 (2C), 129.2, 128.5 (2C), 128.2, 128.1 (2C), 126.5 (2C), 123.4, 116.7, 112.4, 93.8 ppm; HRMS (EI) calcd. for C$_{19}$H$_{14}$N$_{2}$ 270.1157, found 270.1158.

2-phenyl-7-o-tolylpyrazolo[1,5-a]pyridine (8g)
brown liquid; $R_f = 0.48$ (n-hexane/ethyl acetate = 10/1 as eluent); $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.90 (dt, $J = 8.8$, 1.6 Hz, 2H), 7.55 (dd, $J = 8.8$, 12. Hz, 1H), 7.45-7.28 (m, 7H), 7.17 (dd, $J = 8.8$, 6.8 Hz, 1H), 6.88 (s, 1H), 6.67 (dd, $J = 6.4$, 1.2 Hz, 1H), 2.19 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): δ 153.1, 142.1, 140.9, 138.1, 133.9, 133.4, 130.0, 129.1, 128.4 (2C), 128.1, 126.5 (2C), 125.6, 123.1, 116.8, 112.9, 93.7, 19.8 ppm; HRMS (EI) calcd. for C$_{20}$H$_{16}$N$_{2}$ 284.1313, found 284.1314.

2-phenyl-7-m-tolylpyrazolo[1,5-a]pyridine (8h)
brown liquid; $R_f = 0.43$ (n-hexane/ethyl acetate = 10/1 as eluent); $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.58 (dt, $J = 8.8$, 1.2 Hz, 2H), 6.96-6.54 (m, 10H), 6.10 (s, 1H), 2.14 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz): δ 155.4, 147.1, 136.9, 133.8, 131.5, 128.6, 128.2, 128.1, 127.7, 127.4 (2C), 126.8, 126.6 (2C), 105.1, 101.2, 92.5, 21.1 ppm; HRMS (EI) calcd. for C$_{20}$H$_{16}$N$_{2}$ 284.1313, found 284.1314.
2-phenyl-7-p-tolylpyrazolo[1,5-a]pyridine (8i)
brown liquid; \( R_f = 0.43 \) (n-hexane/ethyl acetate = 10/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 8.00-7.96 (m, 4H), 7.51 (dd, \( J = 8.5, 1 \) Hz, 1H), 7.44 (t, \( J = 7.5 \) Hz, 2H), 7.36-7.33 (m, 3H), 7.18 (dd, \( J = 8.5, 7 \) Hz, 1H), 6.89 (s, 1H), 6.83 (dd, \( J = 7, 1.5 \) Hz, 1H) 2.47 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125MHz) : \( \delta \) 152.7, 142.7, 140.4, 139.3, 133.5, 130.7, 129.2 (2C), 128.8 (2C), 128.5 (2C), 126.5 (2C), 123.5, 116.4, 112.1, 93.7 pmm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)N\(_2\) 284.1313, found 284.1311.

7-(2-methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyridine (8j)
White solid; m.p.: 165-167 \( ^\circ \)C; \( R_f = 0.50 \) (n-hexane/ethyl acetate = 10/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 7.91 (dt, \( J = 6.8, 1.6 \) Hz, 2H), 7.57-7.47 (m, 3H), 7.39-7.27 (m, 3H), 7.17-7.08 (m, 3H), 6.86 (S, 1H), 6.76 (dd, \( J = 6.8, 1.2 \) Hz, 1H), 3.79 (S, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 157.8, 142.1, 131.2, 130.6, 128.4 (2C), 128.0, 126.5 (2C), 123.0, 120.5, 116.8, 113.2, 111.6, 93.6, 55.8 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)N\(_2\)O 300.1263, found 300.1263.

X-ray Crystal Data for 8j:

![X-ray Crystal Structure](image)

Empirical formula

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</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0454, wR2 = 0.1279</td>
</tr>
</tbody>
</table>
R indices (all data) \( R_1 = 0.0688, \) wR2 = 0.1535

Largest diff. peak and hole 0.174 and -0.303 e Å\(^{-3}\)

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC XXXXXX.

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].

7-(3-methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyridine(8k)
yellow solid; m.p.: 180-182°C; \( R_f = 0.48 \) (n-hexane/ethyl acetate = 10/1 as eluent);
\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 8.00 (d, \( J = 7.5 \) Hz, 2H), 7.72 (s, 1H), 7.60 (d, \( J = 8 \) Hz, 1H), 7.53 (dd, \( J = 8 \) Hz, 1H), 7.46 (m, 3H), 7.36 (t, \( J = 7.5 \) Hz, 1H), 7.18 (dd, \( J = 8.5, 7 \) Hz, 1H), 7.07 (dd, \( J = 8, 2.5 \) Hz, 1H), 6.90 (s, 1H), 6.87 (dd, \( J = 6.5, 1 \) Hz, 1H)
3.91 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125MHz) : \( \delta \) 159.2, 152.7, 142.7, 140.0, 134.8, 133.4, 129.2, 128.5 (2C), 128.2, 126.5 (2C), 123.4, 121.7, 116.8, 115.3, 114.6, 112.4, 93.8, 55.3 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)N\(_2\)O 300.1263, found 300.1261.

7-(4-methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyridine (8l)
brown liquid; \( R_f = 0.51 \) (n-hexane/ethyl acetate = 10/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 400 MHz) : \( \delta \) 8.05 (dt, \( J = 8.8, 2.0 \) Hz, 2H), 7.98-7.35 (m, 4H), 7.15 (dd, \( J = 8.8, 6.8 \) Hz, 2H), 6.88 (s, 1H), 6.80 (dd, \( J = 6.8, 1.2 \) Hz, 1H), 3.90 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) : \( \delta \) 160.3, 152.6, 142.8, 104.1, 133.4, 130.7 (2C), 128.5 (2C), 128.3, 128.1, 126.5 (2C), 123.6, 116.1, 113.5 (2C), 111.7, 93.7, 55.3 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)N\(_2\)O 300.1263, found 300.1262.

7-(4-nitrophenyl)-2-phenylpyrazolo[1,5-a]pyridine (8m)
orange solid; m.p.: 155-158°C; \( R_f = 0.32 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 8.41 (d, \( J = 9 \) Hz, 2H), 8.28 (d, \( J = 9 \) Hz, 2H), 7.96 (d, \( J = 7 \) Hz, 2H), 7.62 (dd, \( J = 9, 1.5 \) Hz, 1H), 7.45 (t, \( J = 7.5 \) Hz, 2H), 7.38 (t, \( J = 7.5 \) Hz, 1H), 7.23 (dd, \( J = 8.5, 7 \) Hz, 1H), 6.94 (s, 1H), 6.93 (dd, \( J = 7 \) Hz, 1, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125MHz) : \( \delta \) 153.2, 148.0, 142.7, 139.8, 137.8, 132.9, 130.2 (2C), 128.7 (2C), 128.5, 126.5 (2C), 123.4 (2C), 123.3, 118.4, 113.4, 94.5; HRMS (EI) calcd. for C\(_{19}\)H\(_{13}\)N\(_3\)O\(_2\) 315.1008, found 315.1010.

7-hexyl-2-(4-methoxyphenyl)pyrazolo[1,5-a]pyridine (8n)

brown liquid; \( R_f = 0.56 \) (n-hexane/ethyl acetate = 10/1 as eluent); \(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 7.97 (d, \( J = 9 \) Hz, 2H), 7.39 (d, \( J = 8.5 \) Hz, 1H), 7.05 (dd, \( J = 8.5, 7 \) Hz, 1H), 7.00 (d, \( J = 9 \) Hz, 2H), 6.73 (s, 1H), 6.56 (d, \( J = 7 \) Hz, 1H), 3.86 (s, 3H), 3.22 (t, \( J = 7.5 \) Hz, 2H), 1.94 (q, \( J = 7.5 \) Hz, 2H), 1.53 (q, \( J = 7 \) Hz, 2H), 1.43 (m, 4H), 0.94 (t, \( J = 7 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 125MHz) : \( \delta \) 159.6, 152.4, 142.1, 142.0, 127.7 (2C), 126.5, 123.1, 115.0, 114.0 (2C), 109.2, 92.9, 55.2, 31.6, 30.9, 29.1, 26.1, 22.5, 14.0; HRMS (EI) calcd. for C\(_{20}\)H\(_{24}\)N\(_2\)O 308.1889, found 308.1889.

2-(4-methoxyphenyl)-7-phenylpyrazolo[1,5-a]pyridine (8o)

brown solid; m.p.: 158-160°C; \( R_f = 0.52 \) (n-hexane/ethyl acetate = 10/1 as eluent);

\(^1\)H NMR (CDCl\(_3\), 500 MHz) : \( \delta \) 8.07 (d, \( J = 7 \) Hz, 2H), 7.92 (d, \( J = 8.5 \) Hz, 1H), 7.56-7.48 (m, 4H), 7.16 (dd, \( J = 9, 7 \) Hz, 1H), 6.97 (d, \( J = 9 \) Hz, 2H), 6.82 (s, 1H), 6.56 (dd, \( J = 7, 1 \) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 125MHz) : \( \delta \) 159.6, 152.6, 142.7, 140.2, 133.7, 129.3 (2C), 129.2 (2C), 128.1 (2C), 127.7 (2C), 126.2, 123.4, 116.5, 113.9, 112.1, 93.2, 55.2 ppm; HRMS (EI) calcd. for C\(_{20}\)H\(_{16}\)N\(_2\)O 300.1263, found 300.1265.

2,7-bis(4-methoxyphenyl)pyrazolo[1,5-a]pyridine (8p)
green solid; m.p.: 170-172°C; $R_f = 0.54$ (n-hexane/ethyl acetate = 10/1 as eluent); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.05 (d, $J = 9$ Hz, 2H), 7.92 (d, $J = 9$ Hz, 2H), 7.47 (dd, $J = 9$, 1.5 Hz, 1H), 7.15 (dd, $J = 9$, 7 Hz, 1H), 7.07 (d, $J = 8.5$ Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 2H), 6.80 (s, 1H), 6.78 (dd, $J = 7$, 1.5 Hz, 1H), 3.91 (s, 1H), 3.85 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125MHz): $\delta$ 160.3, 159.7, 152.5, 142.8, 140.0, 130.7 (2C), 127.7 (2C), 126.2, 126.1, 123.5, 115.9, 113.9(2C), 113.5(2C), 111.4, 93.1, 55.3, 55.2ppm; HRMS (EI) calcd. for C$_{21}$H$_{18}$N$_2$O$_2$ 330.1368, found 330.1368.

4-(2-(4-methoxyphenyl)pyrazolo[1,5-a]pyridin-7-yl)benzonitrile (8q)

yellow solid; m.p.: 154-156°C; $R_f = 0.42$ n-hexane/ethyl acetate = 10/1 as eluent); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.20 (d, $J = 8.5$ Hz, 2H), 7.88 (d, $J = 8.5$ Hz, 2H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.56 (dd, $J = 9$, 1 Hz, 1H), 7.19 (dd, $J = 8.5$, 7 Hz, 1H), 6.97 (d, $J = 8.5$ Hz, 2H), 6.85-6.83 (2H), 3.59 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz): $\delta$ 159.9, 153.0, 142.7, 138.0, 131.9(2C), 129.8 (2C), 127.7 (2C), 125.7, 123.2, 118.6, 117.9, 114.0 (2C), 112.9, 112.6, 93.7, 55.3; HRMS (EI) calcd. for C$_{21}$H$_{15}$N$_3$O 325.1215, found 325.1212.

7-hexyl-2-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-a]pyridine (8r)

brown liquid; $R_f = 0.51$ n-hexane/ethyl acetate = 10/1 as eluent); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.13 (d, $J = 8$ Hz, 2H), 7.71 (d, $J = 8$ Hz, 2H), 7.44 (d, $J = 9$ Hz, 1H), 7.10 (dd, $J = 9$, 7 Hz, 1H), 6.86 (s, 1H), 6.63 (d, $J = 6.5$ Hz, 1H), 3.22 (t, $J = 8$ Hz, 2H), 1.90 (quintet, $J = 7.5$ Hz, 2H), 1.50 (quintet, $J = 7$ Hz, 2H), 1.38, (m, 4H), 0.93 (t, $J = 7$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz): $\delta$ 150.9, 142.3, 142.1, 137.2, 129.9 (quartet, $J_{C,F} = 64.5$ Hz, 2C), 124.3 (quartet, $J_{C,F} = 270.1$ Hz), 126.6 (2C), 125.5 (quartet, $J_{C,F} = 4.1$ Hz), 123.6, 115.5, 110.1, 94.1, 31.5, 30.9, 29.1, 26.1, 22.5, 14.0 ppm; HRMS (EI) calcd. for C$_{20}$H$_{21}$F$_3$N$_2$ 346.1657, found 346.1658.

S-19
X-ray Crystal Data for 9a:

Empirical formula  \( \text{C}_{38}\text{H}_{42}\text{Cu}_{2}\text{N}_{4} \)

Formula weight  681.84

Temperature  200(2) K

Wavelength  0.71073 Å

Crystal system  Monoclinic

Space group  \( \text{P 2}1/\alpha \)

Unit cell dimensions
\[
\begin{align*}
a &= 14.2593(3) \text{ Å} & = 90^\circ. \\
b &= 12.1166(3) \text{ Å} & = 101.7380(10)^\circ \\
c &= 19.4748(5) \text{ Å} & = 90^\circ.
\end{align*}
\]

Volume  3294.38(14) Å\(^3\)

Z  4

Density (calculated)  1.375 Mg/m\(^3\)
Absorption coefficient 1.324 mm$^{-1}$
F(000) 1424
Crystal size 0.6 x 0.5 x 0.25 mm$^3$
Theta range for data collection 2.14 to 25.35°.
Index ranges -17<=h<=17, -13<=k<=14, -18<=l<=23
Reflections collected 19908
Independent reflections 5936 [R(int) = 0.0637]
Completeness to theta = 25.35° 98.3 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.635 and 0.4947
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 5936 / 0 / 397
Goodness-of-fit on F$^2$ 1.037
Final R indices [I>2sigma(I)] R1 = 0.0432, wR2 = 0.1097
R indices (all data) R1 = 0.0580, wR2 = 0.1192
Largest diff. peak and hole 0.733 and -0.582 e.Å$^{-3}$

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC XXXXXX.
Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].

*X-ray Crystal Data for 9e*
Empirical formula: C\textsubscript{17}H\textsubscript{19}ClCuN\textsubscript{2}O

Formula weight: 366.33

Temperature: 293(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group: P -1

Unit cell dimensions:
\begin{align*}
a &= 9.3101(2) \text{ Å} & = 69.3330(10) \\
b &= 9.2508(3) \text{ Å} & = 84.4530(10) \\
c &= 11.2420(4) \text{ Å} & = 76.7640(10) \\
\end{align*}

Volume: 881.72(5) Å\textsuperscript{3}

Z: 2

Density (calculated): 1.380 Mg/m\textsuperscript{3}

Absorption coefficient: 1.392 mm\textsuperscript{-1}

F(000): 378

Crystal size: 0.6 x 0.42 x 0.15 mm\textsuperscript{3}

Theta range for data collection: 2.25 to 25.05

Index ranges: -11<=h<=11, -10<=k<=11, -13<=l<=13

Reflections collected: 6959

Independent reflections: 3083 [R(int) = 0.0495]

Completeness to theta = 25.05?: 99.1 %
Absorption correction
Semi-empirical from equivalents

Max. and min. transmission
0.7228 and 0.5248

Refinement method
Full-matrix least-squares on $F^2$

Data / restraints / parameters
3083 / 0 / 196

Goodness-of-fit on $F^2$
1.038

Final R indices [$I$>2sigma($I$)]
R1 = 0.0799, wR2 = 0.1958

R indices (all data)
R1 = 0.0866, wR2 = 0.2017

Largest diff. peak and hole
2.787 and -3.062 e.Å$^{-3}$

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC XXXXXX.

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].
Reference


C6H13 6a

\[ \text{HO} \]

[Chemical structure image]

\[ \text{Compound 6a} \]

[Chemical shift data and peaks]

\[ \text{ppm} \]
Pulse Sequence: s2gw
Solvent: CDCl3
Ambient temperature: 25°C
CERNI-200

Pulse 42.0 degrees
Acq. time: 1.195 sec
Width: 3000.0 Hz
12 repetitions

NMR parameters:
1H, 195.175, 200 MHz
DATA PROCESSING
FT extra: MSC
Total time: 2 hr, 51.5 sec
Pulse Sequence: 4200
Solvent: CDCl3
Ambient temperature: 25°C

Pulse 42.0 degrees
Acq. time: 3.002 sec
Width 3000.0 Hz
S/N ratio 10:1

681.5800 MHz, 159.9678376 MHz
501A PROCESSING
FT DATA 32768
Total time 2 hr, 59 min, 36 sec
Mercury-400MM "Hermigyplus400"
Date: Mar 31, 2008
Solvent: CDCl3
Ambient temperature
Total 48 repetitions
Mercury-4000B "Mercuryplus400B"
Date: Mar 31, 2009
Solvent: CCl4
Ambient temperature
Total 3746 repetitions

[Chemical structure diagram of 1g]

[Graph showing 1H NMR spectrum with chemical shifts in ppm]

1g
Solvent: CDCl3
Ambient temperature
GEMINI-200 "oxford200"

Pulse 44.0 degrees
Acq. time 3.002 sec
Width 3000.0 Hz
48 repetitions

Observe H1, 199.8678378 MHz
DATA PROCESSING
FT size 2048
Total time 2 hr, 50 min, 38 sec
1m

NO₂
1n

\[
\begin{align*}
\text{O} & \quad \text{C}_6\text{H}_{13} \\
\end{align*}
\]
Mercury-400D "Mercuryplus400"

Date: Nov 5 2009

Solvent: CDCl3

Ambient temperature

Total 7232 repetitions
WHC-081-2-liquid
Pulse Sequence: 42pul
Solvent: CDCl3
Ambient temperature
Mercury-250 "noyau30e"

8e
Mercury-0808B "Mercuryplus400"
Date: Mar 31 2008
Solvent: CDCl3
Ambient temperature
Total 36 repetitions

8g

18.55 67.63 10.00
10.95 10.30 9.36
28.32
S-100

OMe

8I

Date: Apr 17 2008
Solvent: CEC15
Ambient temperature
Total 48 repetitions

ppm
\[ \text{8q} \]