Supporting Information

A Rare γ-Pyranopyrazole Skeleton: Design, One-Pot Synthesis and Computational study

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1. General Methods

All reagents were purchased from commercial suppliers (Aldrich and Merck) and they were used without further purification unless otherwise noted. The compounds were analyzed by Thermo Science ISQGC-MS and isolated by column chromatography using a hexane-ethyl acetate eluent. $^1$H NMR and $^{13}$C NMR were measured on a Varian VNMRJ 400 Nuclear Magnetic Resonance Spectrometer and chemical shifts were calibrated using residual solvents signals (CDCl$_3$: $\delta$(H) = 7.26, $\delta$(C) = 77) or TMS. Infrared spectra were obtained using a Perkin–Elmer Spectrum 100 by ATR method with neat samples. Melting points were determined by using an Electrothermal Melting Point Apparatus 9200. UV absorption spectra were measured on Shimadzu UV-2550 Spectrophotometer. All computations were carried out with the Gaussian 09 program package. $^1$ Fluorescence experiments were performed by using Varian Cary Eclipse Fluorescence spectrophotometer. Samples were contained in 10.0 mm path length quartz cuvettes (2.0 mL volume). Upon excitation at 250 nm, the emission spectra were integrated over the range 270 nm to 600 nm. The slit width was 10 nm for both excitation and emission. All measurements were conducted at least in triplicate.

2. Experimental Section

Alkynoic acid derivatives were synthesized by using literature methods.$^{[2,3]}$

a. General Method for Synthesis of Pyrazole Compounds

Pyrazole compounds were synthesized by using literature procedure. To a solution of ethyl alkynoate (10 mmol) in absolute ethanol (20 mL) 2 equivalents of hydrazine hydrate (NH$_2$NH$_2$.H$_2$O, 20 mmol 50-60 % in water) was added and solution stirred at reflux temperature for overnight. Then, the solution was cooled to room temperature and the resultant precipitate was filtered with cold ethanol (3 x 50mL).

b. Synthesis of compound (3aa)
To a solution of pyrazol compound (1a) (32 mg, 0.2 mmol) in tetrahydrofuran (2 mL) 1.2 equivalents of phenyl propiolic acid (2) (30 mg, 0.24 mmol) was added and solution stirred for a minute under argon atmosphere. Then, 0.3 equivalent of dimethylaminopyridine (DMAP) (7.3 mg, 0.06 mmol) and 1.2 equivalents of N,N'-dicyclohexylcarbodiimide (DCC) (49.5 mg, 0.24 mmol) were added successively. The progress of reaction was monitored by using thin layer chromatography. When all starting materials consumed the solvent was removed under reduced pressure and the product was isolated by using a short pad of silica as quick as possible.

c. General Method for Synthesis of Flavone Compounds

![Chemical Structure](image)

To a solution of pyrazol compound (1) (0.2 mmol) in tetrahydrofuran (2 mL) 1.2 equivalents of corresponding propiolic acid (2) (0.24 mmol) was added and solution stirred for a minute under argon atmosphere. Then, 0.3 equivalent of dimethylaminopyridine (DMAP) (7.3 mg, 0.06 mmol) and 1.2 equivalents of N,N'-dicyclohexylcarbodiimide (DCC) (49.5 mg, 0.24 mmol) were added successively. The progress of reaction was monitored by using thin layer chromatography. When all starting materials consumed 2 equivalents of Cs₂CO₃ (130.4 mg, 0.4 mmol) was added and the reaction was stirred completion of reaction. Then, solvent was removed under reduced pressure and the resultant residue extracted with dichloromethane (3 x 30 mL). Collected organic layers were dried over Na₂SO₄ and the solvent was evaporated under vacuo. The resultant residue was prufied by slica gel column chromatography.
3. Characterization Data for Synthesized Compounds

5-phenyl-1H-pyrazol-3(2H)-one, (2a)

White solid (85 % yield). Mp: 250-252 °C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) (ppm): 11.16 (bs, 2H), 7.66 (d, \(J=7.6\) Hz, 2H), 7.38 (t, \(J=7.6\) Hz, 2H), 7.28 (t, \(J=7.6\) Hz, 1H), 5.89 (s, 1H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) (ppm): 166.2, 148.6, 135.7, 134.0, 132.5, 132.9, 129.7, 129.9, 92.0. MS (EI, m/z): 160 (100, M\(^+\)), 131 (22), 118 (7), 103 (86), 77 (48). IR (ATR, neat) cm\(^{-1}\): \(\nu\) 1618 [(C=O)], 1500 [(C=C, C=N)].

5-pentyl-1H-pyrazol-3(2H)-one, (2b)

White solid (70 % yield). Mp: 200-202 °C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) (ppm): 10.37 (bs, 2H), 5.22 (s, 1H), 2.41 (t, \(J=7.6\) Hz, 2H), 1.51 (pent, \(J=7.6\) Hz, 2H), 1.30-1.22 (m, 4H), 0.84 (t, \(J=6.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) (ppm): 161.4, 144.8, 88.4, 31.2, 28.8, 26.0, 22.2, 14.3. MS (EI, m/z): 154 (13, M\(^+\)), 125 (4), 111 (25), 98 (100), 67 (9). IR (ATR, neat) cm\(^{-1}\): \(\nu\) 2989 [(C-H)], 1611 [(C=O)], 1543, 1499, 1455 [(C=C, C=N)].

5-phenyl-2-(3-phenylpropioyl)-1H-pyrazol-3(2H)-one, (3aa)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 11.22 (bs, 1H), 7.65-7.62 (m, 4H), 7.52-7.34 (m, 6H), 6.55 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 155.6, 150.6, 144.5, 133.3, 131.1, 129.1, 129.0, 128.9, 128.7, 125.5, 119.1, 93.7, 89.3, 79.8. MS (EI, m/z): 288 (42, M\(^+\)), 259 (10), 232 (14), 206 (22), 193 (7), 129 (96), 116 (16), 102 (100), 89 (17), 77 (33). IR (ATR, neat) cm\(^{-1}\): \(\nu\) 2231 [(C=O)], 1731 [(C=O)].
**2,5-diphenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aa)**

White solid (47.3 mg, 82 % yield). Mp: 200-202 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.02-7.99 (m, 2H), 7.89-7.87 (m, 2H), 7.63-7.54 (m, 3H), 7.49-7.41 (m, 3H), 6.56 (s, 1H), 6.55 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.3, 155.1, 154.3, 152.0, 132.5, 131.5, 129.7, 129.5, 128.7, 126.6, 126.4, 97.0, 87.2. MS (EI, m/z): 288 (3, M+), 260 (2), 231 (2), 203 (2), 155 (1), 129 (18), 102 (100), 77 (17). IR (ATR, neat) cm$^{-1}$: v 1718 [(C=O)], 1620, 1595, 1572 [(C=C, C=N)].

**2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ab)**

White solid (10.6 mg, 25 % yield). Mp: 153-155°C. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.99 – 7.95 (m, 2H), 7.68 (d, J = 6.0 Hz, 1H), 7.48 – 7.41 (m, 3H), 6.49 (s, 1H), 6.17 (d, J = 6.0 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 155.0, 153.4, 153.1, 153.1, 131.3, 129.8, 128.7, 126.6, 100.1, 87.4. MS (EI, m/z): 212 (27, M+), 184 (6), 155 (6), 128 (42), 102 (67), 76 (34), 54 (100). IR (ATR, neat) cm$^{-1}$: v 1726 [(C=O)], 1610, 1595, 1574 [(C=C, C=N)].

**5-methyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ac)**

White solid (25.8 mg, 57 % yield). Mp: 142-144°C. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.98 – 7.95 (m, 2H), 7.47 – 7.41 (m, 3H), 6.41 (s, 1H), 5.94 (s, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 164.7, 154.8, 153.9, 152.3, 131.5, 129.6, 128.7, 126.6, 100.2, 86.7, 19.6. MS (EI, m/z): 226 (10, M+), 197 (7), 155 (2), 141 (3), 127 (5), 102 (41), 76 (18), 53 (100). IR (ATR, neat) cm$^{-1}$: v 1711 [(C=O)], 1624, 1594, 1573 [(C=C, C=N)].
5-pentyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ad)

![Chemical structure](image)

Bright solid (28.2 mg, 50 % yield). Mp: 111-113°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.98 – 7.95 (m, 2H), 7.47 – 7.40 (m, 3H), 6.41 (s, 1H), 5.92 (s, 1H), 2.61 (t, J= 7.6 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.43 – 1.37 (m, 4H), 0.95 – 0.91 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 168.4, 154.8, 154.1, 152.3, 131.5, 129.5, 128.6, 99.3, 86.7, 53.2, 30.9, 26.1, 22.2, 13.8. MS (EI, m/z): 282 (23, M⁺), 239 (3), 226 (8), 207 (10), 197 (100), 161 (11), 123 (15), 102 (41), 67 (100). IR (ATR, neat) cm⁻¹: ν 1718 [(C=O)], 1627, 1591, 1572 [(C=C, C=N)].

2-phenyl-5-((p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ae)

![Chemical structure](image)

White solid (45.3 mg, 75 % yield). Mp: 233-235°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.01 - 7.98 (m, 2H), 7.77 - 7.74 (m, 2H), 7.48 – 7.40 (m, 3H), 7.34 (d, J= 8 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 162.5, 155.0, 154.4, 152.0, 143.4, 131.5, 130.0, 129.6, 128.7, 126.6, 126.2, 96.1, 87.1, 21.6. MS (EI, m/z): 302 (14, M⁺), 274 (10), 207 (10), 151 (6), 143 (45), 115 (95), 102 (100), 76 (41). IR (ATR, neat) cm⁻¹: ν 1717 [(C=O)], 1617, 1591, 1570 [(C=C, C=N)].

5-(4-methoxyphenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6af)

![Chemical structure](image)

Light brown solid (45.8 mg, 72 % yield). Mp: 238-240°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.02 – 7.99 (m, 2H), 7.85 – 7.81 (m, 2H), 7.49 – 7.40 (m, 3H), 7.07 – 7.03 (m, 2H), 6.53 (s, 1H), 6.44 (s, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 163.1, 162.3, 154.9, 152.0, 131.6, 129.6, 128.7, 126.6, 121.7, 114.7, 95.2, 87.0, 55.6. MS (EI, m/z): 318 (5, M⁺), 275 (1), 247 (1), 159 (36), 132 (26), 117 (25), 102 (100), 89 (46), 76 (31). IR (ATR, neat) cm⁻¹: ν 1716 [(C=O)], 1640, 1605, 1572 [(C=C, C=N)].
5-(4-chlorophenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ag)

Pale yellow solid (49.0 mg, 76 % yield). Mp: 235-237°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.00 – 7.97 (m, 2H), 7.82 – 7.79 (m, 2H), 7.54 – 7.52 (m, 2H), 7.48 – 7.42 (m, 3H), 6.54 (s, 1H), 6.50 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.1, 155.2, 154.0, 151.8, 138.9, 131.4, 129.7, 128.7, 127.9, 127.6, 126.6, 97.1, 87.3. MS (EI, m/z): 322 (3, M⁺), 294 (2), 207 (5), 163 (10), 136 (28), 102 (100), 75 (31). IR (ATR, neat) cm⁻¹: ν 1716 [(C=O)].

2-phenyl-5-(o-toly)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ah)

Bright solid (46.5 mg, 77 % yield). Mp: 135-137°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.01 – 7.98 (m, 2H), 7.55 – 7.53 (m, 1H), 7.47 – 7.42 (m, 3H), 7.36 – 7.33 (m, 2H), 6.50 (s, 1H), 6.24 (s, 1H), 2.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 164.4, 155.1, 154.1, 152.2, 136.9, 131.6, 131.5, 131.5, 130.2, 129.6, 129.2, 128.7, 126.6, 126.4, 101.4, 87.1, 20.5. MS (EI, m/z): 302 (18, M⁺), 274 (9), 207 (2), 169 (2), 143 (74), 115 (100), 102 (54), 89 (51), 76 (13). IR (ATR, neat) cm⁻¹: ν 1726 [(C=O)].

2-phenyl-5-(m-toly)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ai)

White solid (42.9 mg, 71 % yield). Mp: 208-210°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.02 – 7.99 (m, 2H), 7.68 – 7.66 (m, 2H), 7.48 – 7.39 (m, 5H), 6.55 (s, 1H), 6.53 (s, 1H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 162.5, 155.0, 154.4, 152.0, 139.2, 133.3, 131.5, 129.7, 129.4, 129.2, 128.7, 126.8, 126.6, 123.5, 96.8, 87.1, 21.2. MS (EI, m/z): 302 (24, M⁺), 274 (26), 245 (4), 230 (5), 207 (17), 143 (100), 115 (80), 102 (60), 89 (23), 73 (36). IR (ATR, neat) cm⁻¹: ν 1711 [(C=O)].
5-(3,5-bis(trifluoromethyl)phenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aj)

White solid (65.3 mg, 77 % yield). Mp: 241-243°C. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.31 (s, 2H), 8.10 – 7.99 (m, 2H), 7.50 – 7.43 (m, 3H), 6.67 (s, 1H), 6.65 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 158.7, 155.6, 153.2, 151.5, 133.3, 133.0, 131.8, 130.0, 128.8, 126.7, 126.3, 125.7, 99.3, 87.8. MS (EI, $m/z$): 424 (13, M$^+$), 396 (16), 367 (2), 339 (2), 327 (5), 299 (9), 271 (14), 238 (8), 169 (23), 155 (6), 127 (9), 102 (100), 77 (21). IR (ATR, neat) cm$^{-1}$: v 1734 [(C=O)], 1625, 1594, 1577 [(C=C, C=N)].

2-pentyl-5-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ba)

Light brown solid (26.5 mg, 47 % yield). Mp: 103-105°C. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.85 (d, $J$= 7.2 Hz, 2H), 7.60 – 7.52 (m, 3H), 6.48 (s, 1H), 6.05 (s, 1H), 2.76 (d, $J$= 7.8 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.39 – 1.35 (m, 4H), 0.91 (t, $J$= 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.0, 158.7, 154.2, 151.4, 132.3, 129.6, 129.2, 126.3, 96.7, 88.8, 31.5, 29.2, 28.6, 22.4, 14.0. MS (EI, $m/z$): 282 (2, M$^+$), 239 (10), 226 (20), 214 (3), 197 (1), 147 (3), 129 (100), 102 (17), 76 (9). IR (ATR, neat) cm$^{-1}$: v 1718 [(C=O)], 1621, 1590, 1576 [(C=C, C=N)].

2-pentyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6be)

Light brown solid (29.6 mg, 50 % yield). Mp: 110-112°C. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.75 – 7.72 (m, 2H), 7.33 (d, $J$= 8.0 Hz, 2H), 6.43 (s, 1H), 6.04 (s, 1H), 2.76 (t, $J$= 7.8 Hz, 2H), 2.45 (s, 3H), 1.77 – 1.69 (m, 2H), 1.39 – 1.34 (m, 4H), 0.90 (t, $J$= 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.2, 158.6, 154.4, 151.4, 143.2, 129.9, 126.7, 126.2, 95.9, 88.7, 31.4, 29.2, 28.6, 22.4, 21.6, 14.0. MS
(EI, m/z): 296 (2, M+), 253 (12), 240 (21), 207 (3), 161 (3), 143 (100), 115 (34), 89 (9), 67 (5). IR (ATR, neat) cm$^{-1}$: $\nu$ 1710 [(C=O)], 1618, 1591 [(C=C, C=N)].

5-(3,5-bis(trifluoromethyl)phenyl)-2-pentyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6bj)

![Chemical structure image]

Bright solid (37.6 mg, 45 % yield). Mp: 163-165°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.28 (s, 2H), 8.09 (s, 1H), 6.61 (s, 1H), 6.16 (s, 1H), 2.78 (t, $J$ = 7.8 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.39 – 1.34 (m, 4H), 0.91 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 159.3, 158.5, 153.2, 151.0, 133.2, 132.9, 131.9, 126.2, 125.6, 121.3, 99.0, 89.5, 31.4, 29.2, 28.5, 22.4, 14.0. MS (EI, m/z): 418 (6, M$^+$), 399 (3), 389 (10), 374 (46), 362 (63), 350 (9), 333 (3), 283 (4), 265 (100), 237 (6), 213 (6), 187 (9), 169 (23), 136 (6), 67(48). IR (ATR, neat) cm$^{-1}$: $\nu$ 1718 [(C=O)], 1629, 1591 [(C=C, C=N)].

5-phenyl-2-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ca)

![Chemical structure image]

White solid (47.1 mg, 85 % yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.90-7.85 (m, 4H), 7.59-7.53 (m, 3H), 7.27-7.25 (m, 2H), 6.53 (s, 1H), 6.51 (s, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 162.2, 155.2, 154.4, 139.8, 132.5, 132.3, 129.5, 129.4, 126.7, 126.3, 96.7, 87.0, 21.4. IR (ATR, neat) cm$^{-1}$: $\nu$ 1716 [(C=O)], 1615, 1595, [(C=C, C=N)].

2-(4-chlorophenyl)-5-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6da)

![Chemical structure image]

White solid (50.3 mg, 90 % yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.92-7.86 (m, 2H), 7.85-7.84 (m, 2H), 7.60-7.55 (m, 3H), 7.42-7.40 (m, 2H), 6.53 (s, 1H), 6.50 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 162.4, 154.2, 153.9, 135.7, 132.6, 130.0, 129.4, 129.3, 129.0, 127.8, 126.3, 96.9, 87.2. IR (ATR, neat) cm$^{-1}$: $\nu$ 1714 [(C=O)], 1620, 1593, [(C=C, C=N)].
**5-phenyl-2-(m-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ea)**

![Chemical Structure Image]

White solid (42.9 mg, 76 % yield). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.89-7.86 (m, 3H), 7.74-7.72 (m, 1H), 7.59-7.53 (m, 3H), 7.36-7.32 (m, 1H), 7.24-7.22 (m, 1H) 6.53 (s, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.3, 155.2, 154.3, 138.5, 132.5, 130.5, 129.3, 128.6, 127.1, 126.3, 123.8, 96.9, 87.2, 21.3 IR (ATR, neat) cm$^{-1}$: $\nu$ 1718 [(C=O)], 1615, 1595, [(C=C, C=N)].

**methyl 4-(7-oxo-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-5-yl)benzoate, (6ak)**

![Chemical Structure Image]

White solid (40.0 mg, 81 % yield). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.22-8.20 (m, 2H), 8.01-7.94 (m, 4H) 7.47-7.43 (m, 3H), 2.41 (s, 3H), 6.62 (s, 1H), 6.58 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 165.8, 161.0, 155.4, 153.9, 133.5, 133.4, 131.3, 130.4, 129.8, 128.8, 126.6, 126.3, 98.4, 87.4, 49.1
4. Fluorescence Absorption and Emission Spectrum of Synthesized Compounds

2,5-diphenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aa)

2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ab)

5-methyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ac)
5-butyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ad)

2-phenyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ae)

5-(4-methoxyphenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6af)
5-(4-chlorophenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ag)

2-phenyl-5-(o-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ah)

2-phenyl-5-(m-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ai)
5-(3,5-bis(trifluoromethyl)phenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aj)

2-pentyl-5-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ba)

2-pentyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6be)
5. Determination of Quantum Yields and Extinction Coefficients

Quantum Yield

Fluorescence quantum yields of synthesized compounds were determined by using optically matching solutions of Coumarin 102 ($\Phi_F=0.76$ in methanol) as a standard.\textsuperscript{[4]} The quantum yield was calculated according to the equation:

$$\Phi_{F(X)} = \Phi_{F(S)} \frac{A_S F_X}{A_X F_S} \left(\frac{n_X}{n_S}\right)^2 \ldots [1]$$

Where $\Phi_F$ is the fluorescence quantum yield, $A$ is the absorbance at the excitation wavelength, $F$ is the area under the corrected emission curve, and $n$ is the refractive index of the solvents used. Subscripts S and X refer to the standard and to the unknown, respectively.

Extinction coefficient

Extinction coefficients of synthesized compounds were calculated by using absorption spectrum of compounds in the range of 1-5 $\mu$M concentration in dioxane solution. The extinction coefficient was calculated according to the equation:

$$A=\varepsilon b c \ldots [2]$$

Where $A$ is the absorbance, $\varepsilon$ is the extinction coefficient ($\text{cm}^{-1} \text{ M}^{-1}$), $b$ is the path length of the sample (cm), and $c$ is the concentration of measured compound (M)
**Table S1:** Absorption and Emission Data for of Pyranopyrazole Compounds

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<th>Compounds</th>
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<th>$\lambda_3$</th>
<th>$\varepsilon_{\lambda_2}$ ($10^4$ M$^{-1}$cm$^{-1}$)</th>
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6. NMR Spectra for All Compounds

$^1$H NMR Spectrum of 2a in DMSO-$d_6$:
$^{13}$C NMR Spectrum of 2a in DMSO-$d_6$: 

![C NMR Spectrum Image]
$^1$H NMR Spectrum of 2b in DMSO-$d_6$: 

![NMR Spectrum of 2b in DMSO-$d_6$](image_url)
$^{13}$C NMR Spectrum of 2b in DMSO-$d_6$: 

[Image of the 13C NMR spectrum with spectral data and peaks labeled]
$^{1}\text{H NMR Spectrum of 3aa in CDCl}_3$: 
$^{13}$C NMR Spectrum of 3aa in CDCl$_3$: 

![C NMR Spectrum](image)
$^1$H NMR Spectrum of 6aa in CDCl$_3$:
$^{13}$C NMR Spectrum of 6aa in CDCl$_3$:
$^1$H NMR Spectrum of 6ab in CDCl$_3$: 
$^{13}$C NMR Spectrum of 6ab in CDCl$_3$:
$^1$H NMR Spectrum of 6ac in CDCl$_3$: 

![NMR Spectrum Image]
$^{13}$C NMR Spectrum of 6ac in CDCl$_3$:
$^1$H NMR Spectrum of 6ad in CDCl$_3$: 

![NMR Spectrum Image]
$^{13}$C NMR Spectrum of 6ad in CDCl$_3$: 
$^1$H NMR Spectrum of 6ae in CDCl$_3$: 
$^{13}$C NMR Spectrum of 6ae in CDCl$_3$:
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$^{13}$C NMR Spectrum of 6af in CDCl$_3$: 
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$^{13}$C NMR Spectrum of 6ag in CDCl$_3$: 
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$^{13}$C NMR Spectrum of 6ah in CDCl$_3$: 
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$^{13}$C NMR Spectrum of 6ai in CDCl$_3$:
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$^{13}$C NMR Spectrum of 6aj in CDCl$_3$:
$^1$H NMR Spectrum of 6ba in CDCl$_3$: 
$^{13}$C NMR Spectrum of 6ba in CDCl$_3$: 

![NMR Spectrum Image]
$^1$H NMR Spectrum of 6be in CDCl$_3$: 

![NMR Spectrum Diagram](image-url)
$^{13}$C NMR Spectrum of 6be in CDCl$_3$: [Image of the spectrum]
$^1$H NMR Spectrum of 6bj in CDCl$_3$: 
\[^{13}\text{C}\] NMR Spectrum of 6bj in CDCl\textsubscript{3}:
$^1$H NMR Spectrum of 6ca in CDCl$_3$: 
$^{13}$C NMR Spectrum of 6ca in CDCl$_3$: 

![Diagram of C NMR Spectrum]
$^1$H NMR Spectrum of 6da in CDCl$_3$: 

[Image of a chemical structure and NMR spectrum]
$^{13}$C NMR Spectrum of 6da in CDCl$_3$:
H NMR Spectrum of 6ea in CDCl₃:
$^{13}$C NMR Spectrum of 6ea in CDCl$_3$: 

![C NMR Spectrum](image)
$^1$H NMR Spectrum of 6ak in CDCl$_3$: 
$^{13}$C NMR Spectrum of 6ak in CDCl$_3$: 
7. Computational Studies

**Figure S1**: Selected interatomic distances (Å) for 3x (3cb).

**Figure S2**: Selected interatomic distances (Å) for 4x.

**Figure S3**: Selected interatomic distances (Å) for 7.
**Figure S4:** Selected interatomic distances (Å) for 3y.

**Figure S5:** Selected interatomic distances (Å) for 4y.

**Figure S6:** Selected interatomic distances (Å) for 6.
Figure S7: Selected interatomic distances (Å) for 3x/4x.

Figure S8: Selected interatomic distances (Å) for 3x/3y.

Figure S9: Selected interatomic distances (Å) for 3y/4y.
Computations at the B3LYP/6-311++G** level

3x (R=H)

-1 1
C  -0.08172700  2.40515300  0.00000000
C   0.87355900  1.35668500  0.00000000
N   0.00000000  0.15894900  0.00000000
C  -1.35357000  1.81425100  0.00000000
N  -1.36039600  0.49129800  0.00000000
O   2.10388600  1.31657000  0.00000000
H  -2.31054500  2.32593600  0.00000000
C   0.36564500 -1.15966600  0.00000000
O   1.50824400 -1.59339400  0.00000000
C  -0.75616200 -2.11140300  0.00000000
C  -1.54145200 -3.02481100  0.00000000
H  -2.26767600 -3.79894400  0.00000000
H   0.16619400  3.45461700  0.00000000

4x (R=H)

-1 1
C  -2.09648500 -0.54360900 -0.12437400
C  -1.31944300  0.68648800  0.01307900
N   0.01132600  0.22252000  0.22029600
C  -1.22678600 -1.60135800 -0.03833300
N   0.02527900 -1.14581200  0.19180900
O  -1.67341800  1.85871100  0.01256800
H  -1.40487500 -2.66482100 -0.11352200
C   1.43159700  0.67135400  0.00893800
O   1.68630200  1.85195900  0.05114800
C   2.26915900 -0.54374000 -0.13260400
H  -3.16623400 -0.57665700 -0.25750600
C   1.38794500 -1.56015600 -0.03296200
H   1.53588000 -2.63471200 -0.05918700

7 (R=H)

0 1
C   -2.12330800 -0.53409900 -0.11932800
C   -1.34241400  0.70777000  0.00956100
N   0.00002800  0.23163500  0.22948700
C  -1.28544900 -1.59171400 -0.03521900
N  -0.00010300 -1.14732800  0.19872800
O  -1.67088100  1.86520400 -0.03581800
H  -1.47985800 -2.65195300 -0.09289100
C   1.34255500  0.70760200  0.00968700
O   1.67121000  1.86498200 -0.03573300
C   2.12321800 -0.53439300 -0.11933000
H  -3.19224800 -0.55345300 -0.24921900
C   1.28514100 -1.59186200 -0.03547900
H   1.47936600 -2.65212600 -0.09325200
H   3.19217000 -0.55392400 -0.24909700
3x-TS-4x (R=H)

-1 1
C   -2.11987200 -0.69293100  -0.00019300
C   -1.39040300  0.54408700  -0.00007400
N   -0.00680000  0.09636800  0.00022600
C   -1.18588500 -1.72221600  0.00016500
N   0.07073700  -1.27451800  0.00007400
O   -1.75054200  1.71892500  0.00040300
H   -3.16219000  2.79107900  0.00055300

3x-TS-3y (R=H)

-1 1
C    2.21407200   0.26800700   0.44697600
C    1.04970300   0.88107800  -0.09595800
N    0.25598300  -0.25694600  -0.46953400
C    1.98001400  -1.11474100   0.45386200
N    0.80742300  -1.48088200  -0.05384300
O    0.67908200   2.05711300  -0.27402700
H    2.64682000  -1.89468800   0.80674700
C   -1.15110500  -0.22320200  -0.60797900
O   -1.73078700  -0.33453300  -1.66306700
C   -1.88928800  -0.50024000   0.63548400
C   -2.49544800   0.10945000  1.66445200
H   -3.01152600   0.25524000   2.58076900
H    3.08681700   0.80019300   0.79184800

3y-TS-4y (R=H)

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C    2.01203400  -0.87039800  -0.00000800
C    0.61503700  -0.92803700   0.00001100
N    0.19605200   0.43607900  -0.00002300
C    2.33016600   0.50154200   0.00003300
N    1.27705200  -1.29915500  -0.00002600
O   -0.17452300  -1.93869000   0.00010600
H    3.31714600   0.94870100  -0.00005900
H    2.67348300  -1.72156700  -0.00000200
C   -1.12377900   0.94598600  -0.00001200
C   -2.14857600  -0.09340300  -0.00013400
O   -1.33555200   2.14486600   0.00010500
C   -1.98946100  -1.33818900  -0.00003800
H   -2.39428800  -2.32818600   0.00000000
3x (R=Methyl)

-1 1
C  -2.58098000  0.16499400  -0.00006800
C  -1.78676900  -1.00816000  -0.00004800
N  -0.41828700  0.44072800  0.00006400
C  -1.71550600  1.27365900  0.00001800
N  -0.42911000  0.95955600  0.00009300
O  -2.03835200  -2.21341600  -0.00010500
C   0.78176000  -1.10301900  -0.00006700
O   0.92906000  -2.31789500  0.00008800
C   0.78176000  -1.10301900  -0.00006700
H   3.66010900  0.16693300  -0.00014300
C   2.10252500  2.72365100  0.00001900
H   2.70259800  2.97379000  0.88251200
H   2.70229600  2.97387500  -0.88265500
H   1.20484700  3.34633700  0.00020100
C   4.28030500  1.07396500  -0.00009300
H   4.88282900  0.83197500  -0.88234400
H   4.88227600  0.83305500  0.88283100
H   4.10375100  2.15485600  -0.88283100

4x (R=methyl)

-1 1
C  -0.17714900  2.09541500  0.08785300
C  -1.36133500  1.25413500  -0.02414800
N  -0.82686800  -0.0441900  -0.22738800
C   0.93893900  1.29937400  -0.00297300
N   0.54941100  0.01075600  -0.21887400
O  -2.55150400  1.54441200  0.01576100
C  -1.21433400  -1.46467100  0.02441600
O  -2.38516400  -1.76613500  0.09708300
C   0.02794300  -2.25135000  0.12329400
H  -0.20013100  3.16816700  0.20502800
C   1.02479800  -1.34819900  0.00451100
C   2.37559600  1.70946500  0.08167300
H   2.43955300  2.79861500  0.10756600
H   2.94997300  1.34955100  -0.77587100
H   2.85435700  1.31916000  0.98483000
C   2.50611500  -1.57375400  -0.00646700
H   2.67188100  -2.64679500  0.08731000
H   3.02262800  -1.07339000  0.82292800
H   2.97383500  -1.22837500  -0.93825700

7 (R=methyl)

0 1
C   0.07880800  -2.11680700  0.09718900
C   1.31268800  -1.33335800  -0.00673700
N   0.83334800  0.00007400  -0.23656400
C  -0.99977900  -1.30035000  -0.00459000
N  -0.55339000  -0.00003700  -0.22881100
O   2.47346400  -1.65435600  0.06116000
C   1.31244400  1.33337600  -0.00548000
O   2.47318500  1.64743700  0.04074100
C   0.07846400  2.11685100  0.09700500
H   0.06399100  -3.18743300  0.21869900
C   -0.99999600  1.30020900  -0.00461700
H   0.06349700  3.18754400  0.21790800
C   -2.45020300  -1.64743700  0.04074100
H   -2.55789400  -2.72894000  0.11614500
H   -2.96979900  -1.31243900  -0.86076200
C   -2.45047300  1.64710700  0.04042500
H   -2.55833200  2.72862400  0.11614500
H   -2.94822400  1.19703300  0.90365600
H   -2.96992100  1.31168100  -0.86076200

3y (R=methyl)

-1 1
C   1.90904600  -1.37763100  0.00007400
C   0.51502800  -1.15802500  0.00004000
N   0.43797800  0.32034600  -0.00006000
C   2.53622200  -0.11631600  0.00003800
N   1.69888600  0.91004400  -0.00008400
O  -0.47589700  -1.89862400  0.00009900
C  -0.67583200  1.12462300  0.00003900
O  -0.64108800  2.35190700  0.00012600
C  -1.96531200  0.44994700  -0.00008000
C  -3.10513500  0.05813600  -0.00003700
H   2.37297600  -2.35192900  -0.00005500
C   4.01097000  0.15931000  -0.00004900
H   4.49549700  -0.27434200  -0.88257000
H   4.49547100  -0.27419900  0.88255500
H   4.18377600  1.23774800  -0.00013800
C  -4.42724100  0.54715200  -0.00007400
H  -5.00235900  -0.24699600  -0.88249900
H  -5.00239400  -0.24704900  0.88269700
H  -4.35161200  -1.63972400  -0.00010800

4y (R=methyl)

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C  -1.35568400  -1.45029400  -0.00807100
C  -0.12605300  -0.81295600  -0.00593000
N  -0.35345300  0.53646600  0.00453700
C  -2.28796700  -0.38223600  0.00185000
N  -1.69756600  0.80721800  0.00867000
O   1.09766400  -1.32270300  -0.01272100
H  -1.53643300  -2.51314400  -0.01484300
C   0.71189900  1.53748200  -0.00070500
C   2.06030200  0.98879600  0.00817200
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3x-TS-4x (R=methyl)

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N  0.46738600  0.74265100  1.00017900
C  2.08141500 -0.66292800 -0.15248500
N  1.18016300 -0.03413200  1.00017900
O  0.25646200  1.67853300  1.00017900
C  -0.85827300  0.97240700  1.00017900
O  -1.17057800  1.90373000  1.00017900
C  -1.83600000 -0.00000000  1.00017900
C  -2.63527800  0.81086000  1.00017900
H  2.57348000 -0.18827000  1.00017900
C  3.10239000 -1.67853300 -0.57597900
H  2.85965000 -1.05097000  1.00017900
H  3.13127200 -2.56503000  1.00017900
H  4.11068400 -1.24796100  1.00017900
C  -3.57263300  1.79516200  1.00017900
H  -3.54867900  1.80922200  1.00017900
H  -3.31022900  2.79970100  1.00017900
H  -4.59988200  1.58480200  1.00017900

3y-TS-4y (R=methyl)

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C  1.38784800 -1.46666700  0.00002500
C  0.11830600 -1.89086000  0.00000700
N  0.33866000  0.50140900  0.00002700
C  2.29357800 -0.37963100  0.00000200
N  1.68888800  0.79661500  0.00031500
O  -1.04882400 -0.44287400  0.00008300
H  1.80066500 -2.52417900  0.00009700
C  -0.64450800  1.52745800  0.00003100
C  -2.01721200  1.03800600  0.00001100
O  -0.30754300  2.69856800  0.00002700
C  -2.37882400  0.18020600  0.00002200
C  3.79184100  0.43988600  0.00000700
H  4.17065900 -0.96764200  0.88289600
H  4.19910700  0.57323700  0.00004300
H  4.17065900  0.96832600  0.88249900
C  -3.54295700 -1.08778100  0.00010600
H  -4.49893300  0.49409830  0.00009200
H  -3.53540200  1.73642000  0.88132900
H  -3.53553000  1.73600100  0.88185700
8. Proposed reaction mechanism

![Proposed reaction mechanism diagram](image)

**Figure S10:** Proposed reaction mechanism

**Table S2: Reaction Energy, ΔG and k**

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<tr>
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<tr>
<td>12 3x -&gt; 3x-TS-3y</td>
<td>12.69</td>
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<tr>
<td>13 3y -&gt; 3x-TS-3y</td>
<td>13.57</td>
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<td>14 3y -&gt; 3y-TS-4y</td>
<td>14.43</td>
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<td>15 4y -&gt; 3y-TS-4y</td>
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<table>
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<th>Reaction Barrier kcal/mol</th>
<th>R=H</th>
<th>R=Methyl</th>
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<td>17 3x -&gt; 3y</td>
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<td>18 3y -&gt; 4y</td>
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Figure S11: Electron density potential map of compound 3cb

9. X-Ray Diffraction Analysis

For the crystal structure determination, single-crystal of compound 6aa was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and oscillation scans technique with Δω = 5° for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with F^2 > 2σ(F^2). Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc.,2005) software. The structures were solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the program SHELXL-97. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. Crystal data for 6aa: C_{18}H_{12}N_{2}O_{2}, crystal system, space group: monoclinic, P2_1/n; (no:14); unit cell dimensions: a=4.7369(4), b=24.6856(22), c=12.2902(13) Å, α= 90, β = 99.492(3), γ = 90 °; volume: 1417.46(8) Å³; Z = 4; calculated density: 1.35 g/cm³; absorption coefficient: 0.090 mm⁻¹ ; F(000)= 600; θ-range for data collection 2.9–28.2°; refinement method: full matrix least-square on F^2; data/parameters: 3508/200; goodness-of-fit on F^2: 1.002; final R-indices [I > 2σ(I)]: R₁ = 0.045, wR₂ = 0.101; largest diff. peak and hole: 0.177 and -0.135 e Å⁻³.

CCDC-1456335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
**Figure S11:** Packing diagram viewed dawn along the diagonal [101] axis

**SUPPLEMENTARY DATA for compound 6aa**

Fractional atomic coordinates and isotropic temperature factors (Angstrom squared), with standard deviations in the least significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors are shown.

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<th>y/b</th>
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H(11) 0.60821 0.37078 0.46776 0.06119
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C(15) 1.1447(5) 0.2316(1) 0.5284(2) 0.08502
H(15) 1.13862 0.21917 0.59940 0.10202
Vibration parameters (Angstrom squared) in the expression: $-2\pi^2(U_{11}(h.a^*)^2 + U_{22}(k.b^*)^2 + U_{33}(l.c^*)^2 + 2U_{12}.h.k.a^*.b^* + 2U_{13}.h.l.a^*.c^* + 2U_{23}.k.l.b^*.c^*)$

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C(10) - O(1) - C(7) - C(8)   0.1
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N(2) - N(1) - C(10) - O(1)  179.7
C(10) - N(1) - N(2) - C(12)  0.6
N(2) - N(1) - C(10) - C(11) -0.4
N(2) - N(1) - C(9) - O(2)   -1.5
N(2) - N(1) - C(9) - C(8)   179.4
C(9) - N(1) - N(2) - C(12)  -178.8
C(9) - N(1) - C(10) - O(1)  -1.0
C(10) - N(1) - C(9) - O(2)  179.2
C(10) - N(1) - C(9) - C(8)   0.1
C(9) - N(1) - C(10) - C(11)  178.9
N(1) - N(2) - C(12) - C(11) -0.6
N(1) - N(2) - C(12) - C(13)  178.0
O(1) - C(7) - C(1) - C(2)  -173.1
O(1) - C(7) - C(1) - C(6)   7.3
O(1) - C(7) - C(8) - H(8)   179.0
O(1) - C(7) - C(8) - C(9)  -1.0
C(1) - C(7) - C(8) - H(8)  -1.9
C(1) - C(7) - C(8) - C(9)  178.1
C(8) - C(7) - C(1) - C(2)  7.7
C(8) - C(7) - C(1) - C(6) -171.9
C(1) - C(2) - C(3) - C(4)  0.7
H(2) - C(2) - C(3) - H(3)  0.7
H(2) - C(2) - C(3) - C(4) -179.3
C(12) - C(13) - C(18) - H(18)  1.5
C(12) - C(13) - C(18) - C(17) -178.5
C(12) - C(13) - C(14) - H(14) -1.6
C(12) - C(13) - C(14) - C(15)  178.4
C(14) - C(13) - C(18) - H(18) -179.5
C(18) - C(13) - C(14) - H(14)  179.4
C(14) - C(13) - C(18) - C(17)  0.4
C(18) - C(13) - C(14) - C(15) -0.6
C(1) - C(6) - C(5) - C(4)  0.7
C(1) - C(6) - C(5) - H(5) -179.3
H(6) - C(6) - C(5) - C(4) -179.2
H(6) - C(6) - C(5) - H(5)  0.8
C(2) - C(3) - C(4) - H(4)  179.9
C(2) - C(3) - C(4) - C(5) -0.1
H(3) - C(3) - C(4) - H(4) -0.1
H(3) - C(3) - C(4) - C(5)  179.9
C(3) - C(4) - C(5) - C(6) -0.6
C(3) - C(4) - C(5) - H(5)  179.4
H(4) - C(4) - C(5) - C(6)  179.4
H(4) - C(4) - C(5) - H(5) -0.6
C(13) - C(18) - C(17) - C(16) -0.1
C(13) - C(18) - C(17) - H(17)  179.9
H(18) - C(17) - C(16)  179.9
H(18) - C(17) - H(17)  -0.1
C(13) - C(14) - C(15) - C(16)  0.3
C(13) - C(14) - C(15) - H(15)  -179.7
H(14) - C(15) - C(16)  -179.7
H(14) - C(15) - H(15)  0.3
H(16) - C(17) - C(18)  179.8
H(16) - C(17) - H(17)  -0.1
H(16) - C(15) - C(14)  -180.0
H(16) - C(15) - H(15)  0.0
C(15) - C(17) - C(18)  -0.2
C(17) - C(15) - C(14)  0.1
C(15) - C(17) - H(17)  179.8
C(17) - C(15) - H(15)  -180.0

Complete Listing of Torsion Angles (Angstroms)

<table>
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<tr>
<th>Angle</th>
<th>Value</th>
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<tbody>
<tr>
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<td>O(1) - C(10)</td>
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<td>O(2) - C(9)</td>
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<td>C(1) - C(2)</td>
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<td>C(1) - C(6)</td>
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<tr>
<td>C(10) - C(11)</td>
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**Complete Listing of Torsion Angles (Degrees)**

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<th>Angle</th>
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<tbody>
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<td>118.4(2)</td>
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<tr>
<td>C(10)-C(11)-H(11)</td>
<td>128.1(2)</td>
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</table>
10. References


(5) Rigaku/MSC, Inc.: 9009 new Trails Drive, The Woodlands, TX 77381.

(6) Sheldrick, G. M. SHELXS97 and SHELXL97; University of Göttingen: Germany, 1997.